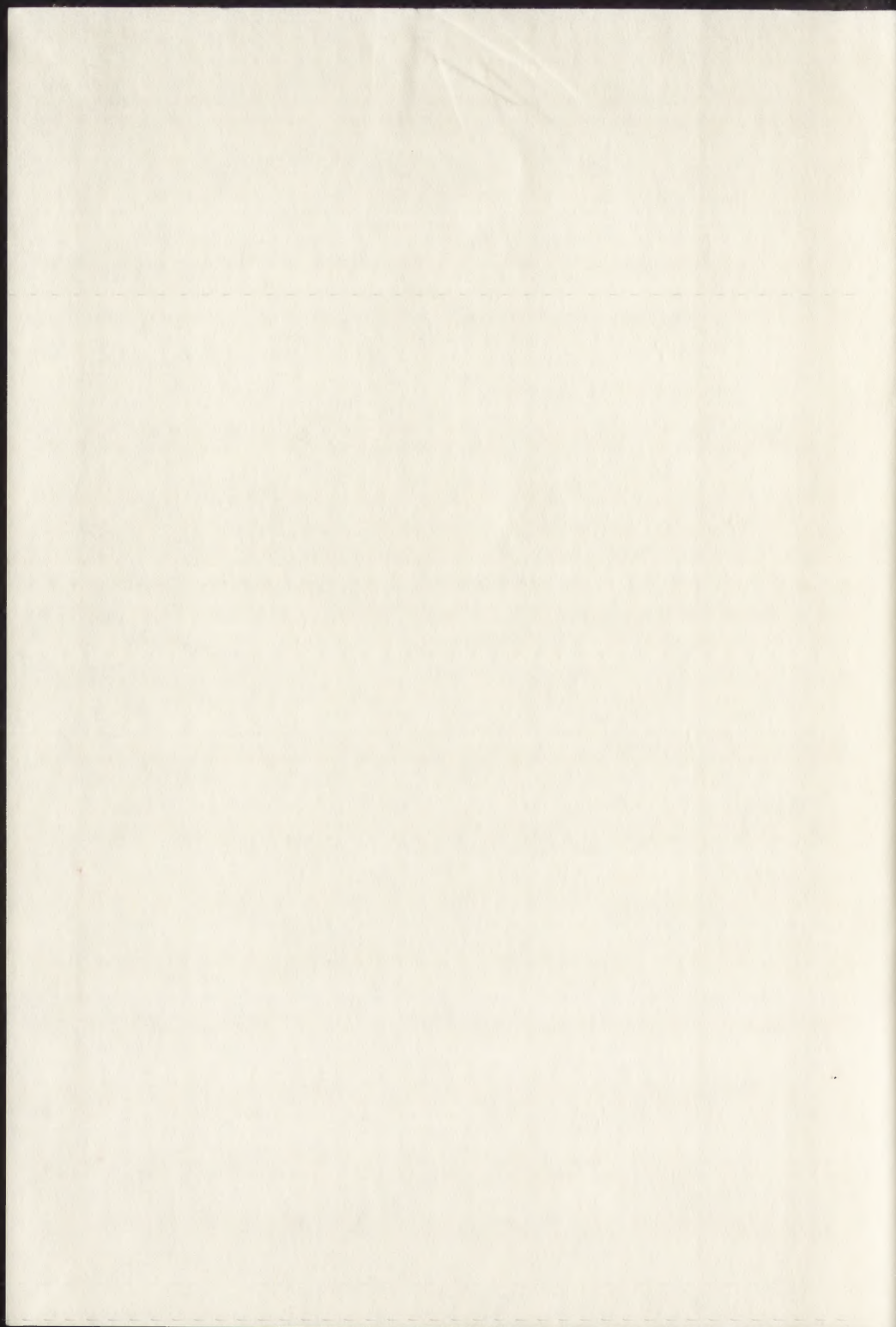


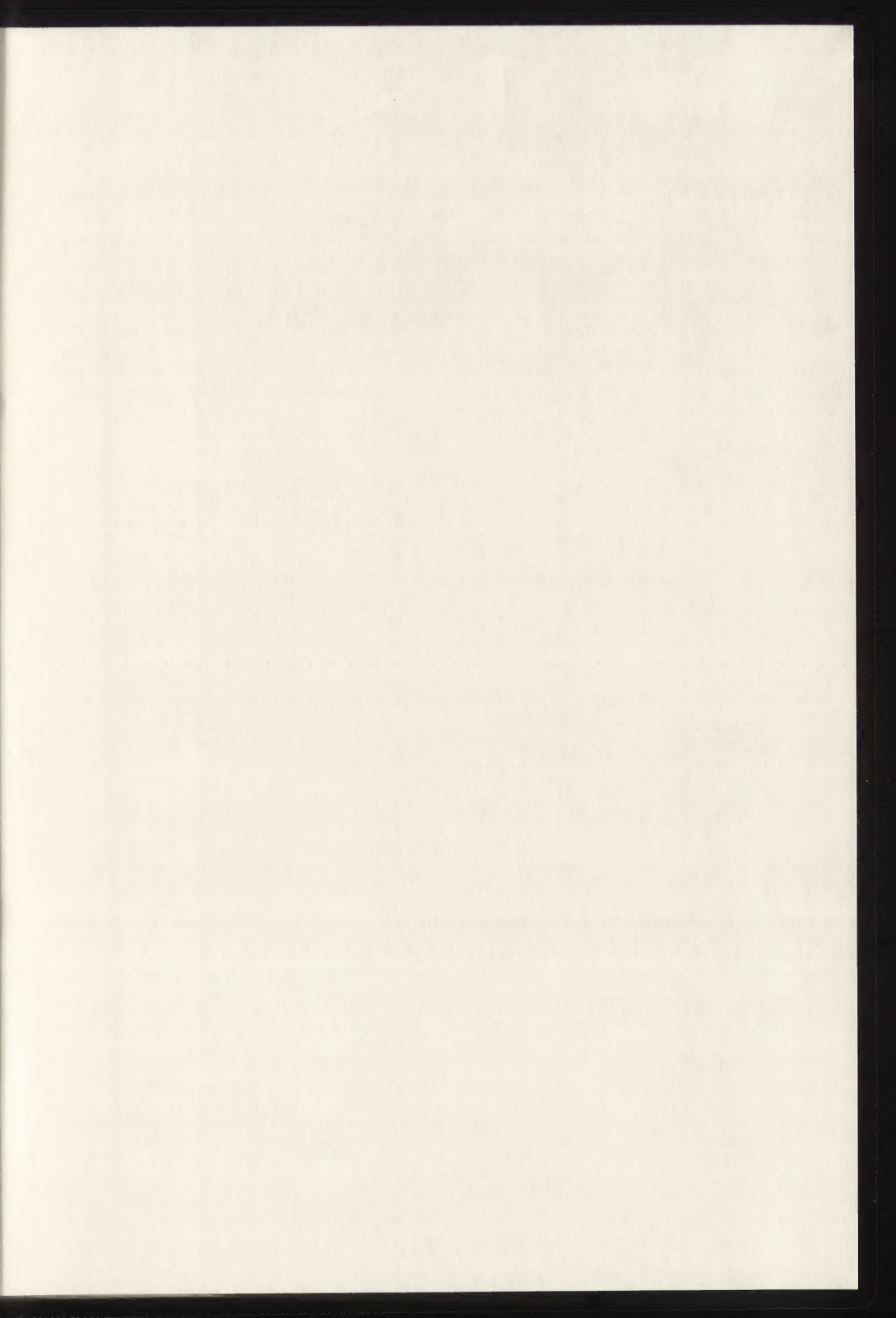
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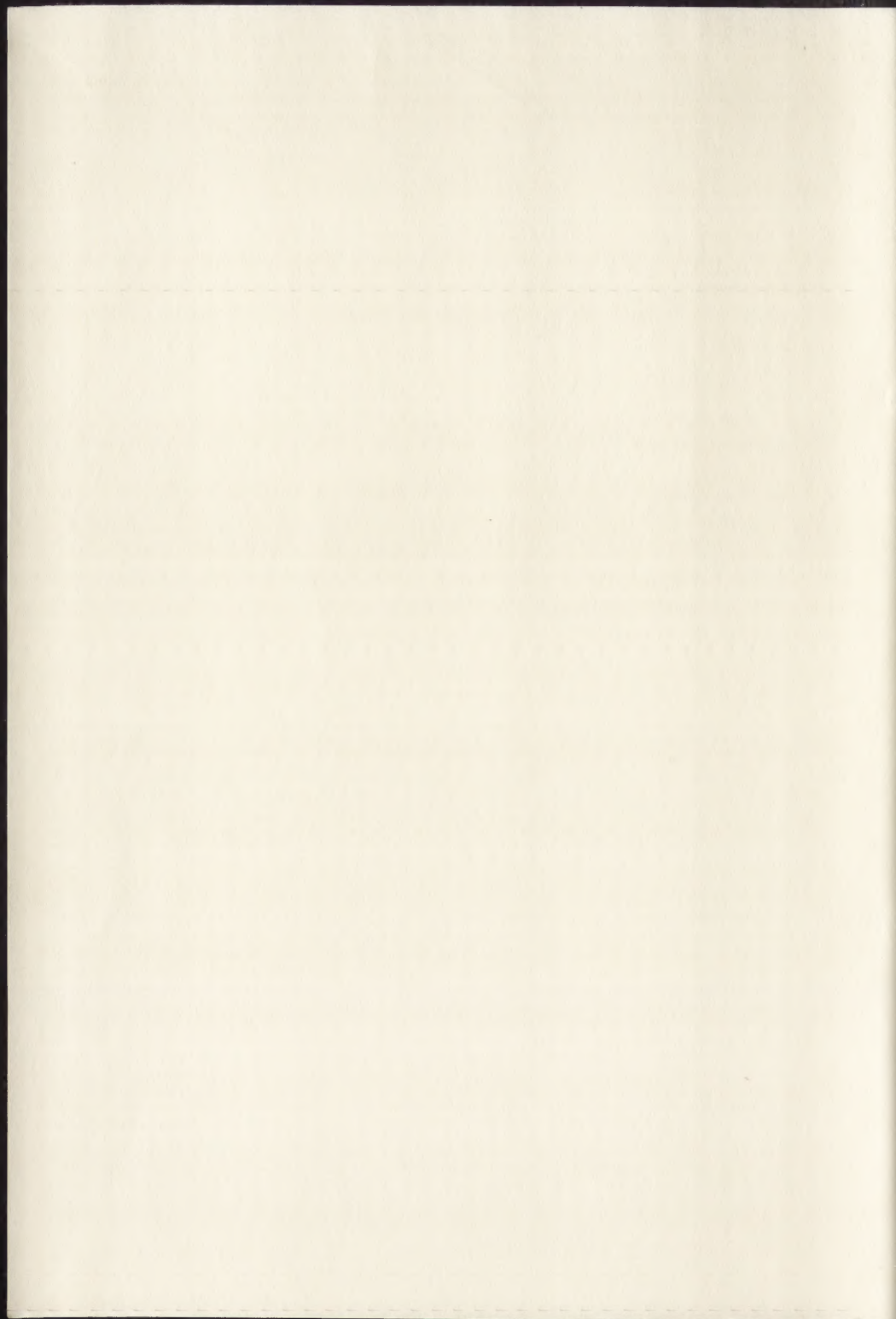


*Why ask for the moon
When we have the stars?*









THE CONSERVATION OF WATERLOGGED TIMBER AT KETELHAVEN

(HOLLAND)

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1. Introduction

After a large flood in the Zuiderzee area at the beginning of this century the dutch government decided to sepearate the Zuiderzee from the Northsea with a barrier dam and to create five polders in the fresh water lake, the IJsselmeer, which was going to be formed (fig. 1).

The aim in making these polders was the extension of the area of land available for agricultural use. During the last two decennia there has been a change anagricultural development of the polders into a miltipurpose development in which urbanisation, agricultural exploitation, recreation and preservation of area's of high biological interest have become important factors. Two polders have been completed, two are being developed now (Flevoland) and the fifth still has be made.

During the development of the polders many wrecks of ships have been found. A number has been excavated. Since the conservation of the finds of this size, entire ships or big parts thereof, causes numerous problems with respect to the conservation in january 1973 a board experts with experience in the field of wood and waterlogged wood conservation has been formed. The task of this board being to advise the IJsselmeerpolders Development Authority with respect to the conservation of these big objects consisting of waterlogged timber.

At about the same time the first Roman ships at Zwammerdam have been found and the IJsselmeerpolders Development Authority was, because of its experience in excavating ships, asked to do the excavation. At Zwammerdam 6 wrecks and a rudder dating from roman time were found.

The biggest ship was about 34 m long, two others about 20 m. The three small boats have lengths varying between 5 and 10 m. During the excavation of the ships it was decided that the conservation and restauration should take place at the workshop of the Ketelhaven museum. Since the size of this find far exceeded the then existing concervation capacity a new conservationplant had to be built for the conservation process advised by the board of experts. In summer 1974 two ships have been found at Utrecht which after

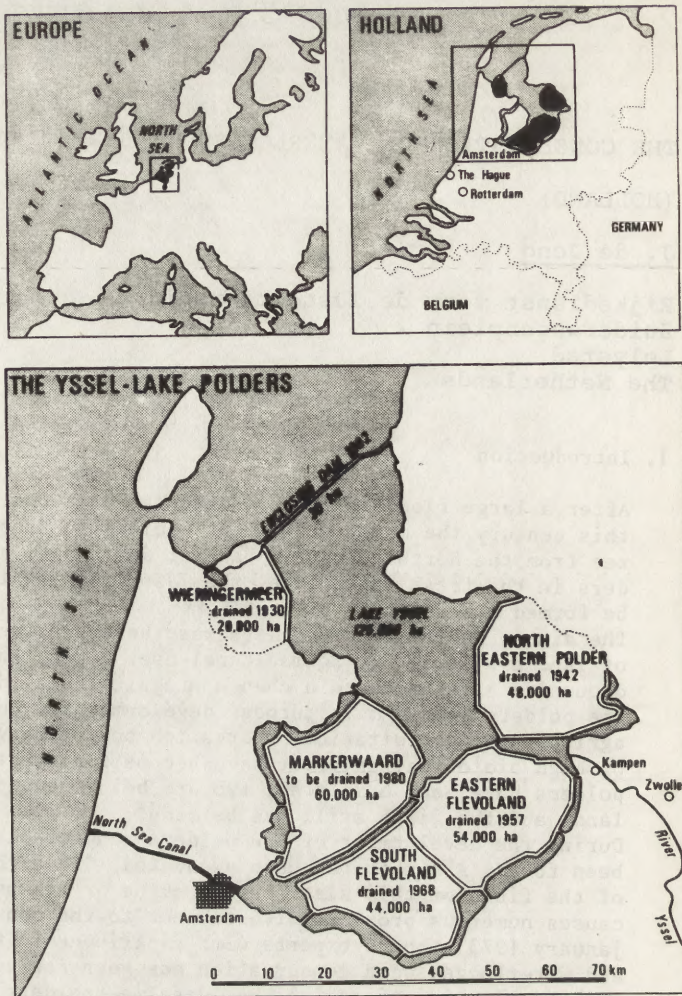


fig. 1. The IJsselmeerpolders development project

excavation have been transported to Ketelhaven. One is going to be conserved and reconstructed, the other partly. As well in the Zwammerdam as in the Utrecht find, european oak is mainly used as the construction material.

2. The aim of the conservation

Since the objects to be conserved are unique the process should be safe. There should be a reasonable safety that a good final product will result, or the entire process should be reversible.

The aim of any conservation process for waterlogged wood should be the stabilization of the dimensions of the find in such a way that it can be kept at normal museum conditions (in the Ketelhaven museum this will be 60-70% r.h.; 18-20°C). If the timber is highly degraded an improvement of the mechanical properties of the wood next to the dimensional stabilization may be necessary. Both dimensional stabilization and improvement of mechanical properties of the wood can be achieved by an exchange of the water in the waterlogged wood for other chemicals such as salts, monomers or polymers (1). These chemicals should remain in the wood, exert no stresses when subject to changing environmental conditions and should not act as a nutrient source for micro-organisms. Finally the process should be as simple and harmless as possible. It was regarded desirable that the conservation process could be automatized.

Since time lacked to develop new conservation processes, the board of experts decided to review the existing few possibilities for the conservation of big objects of waterlogged timber in order to decide which process should be preferred in this case. Also the research for new methods for the dimensional stabilization of large objects of waterlogged timber was stimulated.

3. Possible processes and the conservation process for the Zwammerdam ships.

The following conservation processes have been studied and compared with each other:

1. Freeze-drying of waterlogged wood,
2. Impregnation of waterlogged wood with glycolmethacrylate,
3. Exchange of the water with a volatile, water mixcable organic solvent followed by impregnation of the dehydrated wood,
4. Impregnation with polyethyleneglycol.

These four possibilities will be reviewed briefly, the method chosen and research results pertaining to this method will be discussed.

Freeze-drying

By freezing the waterlogged timber before the evaporation of the water starts the problems of cell-collapse and shrinkage of the wood can be avoided. However due to the expansion of water on freezing damage of the object can occur. Ambrose (2) avoided these problems by impregnating the wood with a small amount of polyethyleneglycol 400 (PEG 400) before freeze-drying. He also suggested that the process might be simplified by eliminating the vacuum-tank by drying the timber instead with a stream of very dry air. Brorson Christensen (3) developed a modified freeze-drying technique. The water in the timber is exchanged for tertiary butyl-alcohol, which is removed by freeze-drying.

After freeze-drying following the Ambrose method the object contains just enough P.E.G. 400 for dimensional stabilization. No improvement of mechanical properties has been achieved. After the freeze-drying from tertiary-butylalcohol the timber will behave like a hygroscopic substance and a final treatment will be needed to obtain a durable dimensional stabilization and, if needed, improvement of strength. Heslinga (5) stated that drying methods

have a disadvantageous effect on a P.E.G.-impregnation afterwards. Freeze-drying techniques require high investments in equipment and highly skilled labour. The process is difficult to automatize.

Impregnation with glycolmethacrylate

This method, which is based on the exchange of water in the waterlogged timber, for the water miscible monomer glycolmethacrylate has been described by Munnikendam (4).

This process results in both dimensional stabilization and strength improvement of the object. The process, which seems highly promising, has, however, until now only been applied to rather small objects.

Exchange of water with a volatile water miscible organic solvent followed with impregnation of dehydrated wood

Several techniques have been developed based upon this principle (1, 3, 6, 7). First there is the alcohol-ether-method where a succession of the liquids as alcohol, toluene and diethylether is used. This method has only been applied to small objects. Mc. Kerrel (8) describes a method where the water in the timber is replaced by acetone. Combined treatment with acetone and hydrochloric acid increased the impregnation of the timber with synthetic (PEG) or natural polymers (Rosin).

Based on the freeze-drying from tertiarybutylalcohol Brorson-Christensen (3) developed a modified technique. Here the water is replaced by tertiarybutylalcohol which is followed by an impregnation with a solution of PEG 4000 in tertiarybutylalcohol at 50-55°C. After this treatment the tertiarybutylalcohol is removed by freeze-drying. This technique is being used now for the treatment of large objects in Denmark. Results are not yet available. It is said to be applicable to all species of wood and all types of degradation.

Impregnation with polyethyleneglycol

For impregnation of wood: polyethyleneglycols with molecular weights from about 1000 to 4000 are regarded as most suitable. PEG's with a molecular weight under 1000 are too hygroscopic and may, if present in excess compared to the amount which can be absorbed to the wood material, cause bleeding out of PEG-water solutions. Going from a molecular weight from 1000 to 4000 these problems become less, impregnation however becomes more difficult. If improvement of the mechanical properties of the timber is desirable a wax-like PEG should be used.

For the impregnation of PEG in waterlogged timber two methods have been described: spraying and treatment with cold or warm (65°C) baths.

Spraying is technically simple to realize, the objects can be treated as a whole. It may however be difficult to reach every part of the object. Since spraying is carried out with rather low concentrations of PEG (PEG 1500 at the Wasa) the impregnation at high relative humidity conditions will be very slow.

Since we know from experiments with impregnation baths (PEG 4000, 65°C, concentration going up from 10% to 60% in 1½ year) that in rather sound big pieces of oak PEG has been transported inward for just the other few centimeters it can be expected that with

the spraying technique the time needed to achieve satisfactory treatment will be very long, as Noack has stated (8,9).

When waterlogged wood is treated with warm baths, the impregnation is speeded up. A higher molecular grade PEG can be used, which offers an advantage with respect to the hygroscopicity of PEG. Problems may occur, especially with (northern) European oak which is not highly degraded.

In that case shrinkage during the impregnation may occur, due to water leaving the timber faster than PEG penetrating and also shrinkage, cracking and warping of the timber during the drying afterwards due to insufficient impregnation will occur. Since the Zwammerdam and Utrecht ships consist mainly of European oak carefull attention should be given to this point.

Brorson Christensen (3) and Morén (10) have given classifications of oak in order to indicate which process for PEG-treatment can be used. Based on their classifications the following can be said with respect to oak timber quality and PEG impregnation possibilities.

class 1. Highly degraded oak

The material is very soft and has a water content above 80% based on the wet material (or 400% or more if based on the dry material of the waterlogged wood). The timber has lost almost all cellulose and shows a volume shrinkage up to 70% on drying.

This wood can be treated with PEG 4000 in warm solutions giving good results.

class 2. Medium degraded oak

The material contains, based on the wet weight, 65%-80% water. This wood will also show upon drying considerable shrinkage and cracking. Treatment with warm PEG 4000 solutions caused shrinkage during the process, which can be avoided with a cold treatment as described by Brorson Christensen (3).

class 3. Slightly degraded oak

The water content of this timber is less than 65% (based on wet weight) or less than 185% is based on the dry material. There is almost no possibility of obtaining satisfactory impregnation of timber with PEG 4000 of oak this quality as is shown in fig 2.

From this figure it can be seen that the size of the object highly influences the results. In small sample blocks (10 x 5 x 5 cm) the results are much better than in medium sized objects (0,10 x 0,15 cm and length up to 3 m) which in turn are better impregnated than hull plankings and knees. The treatment given was a hot bath process. Temp. 60°C. The PEG 4000 concentration was raised from 10% up to 60% in a period of 18 months. The watercontent of the samples varied between 50 and 60%.based on wet wieght.

It will be clear that, since often two or three of these quality classes occur in one piece of oak timber, carefull attention should be paid to the distribution of timber quality throughout the object. Generally the best quality (the lowest watercontent areas), which is present will determine the treatment process to

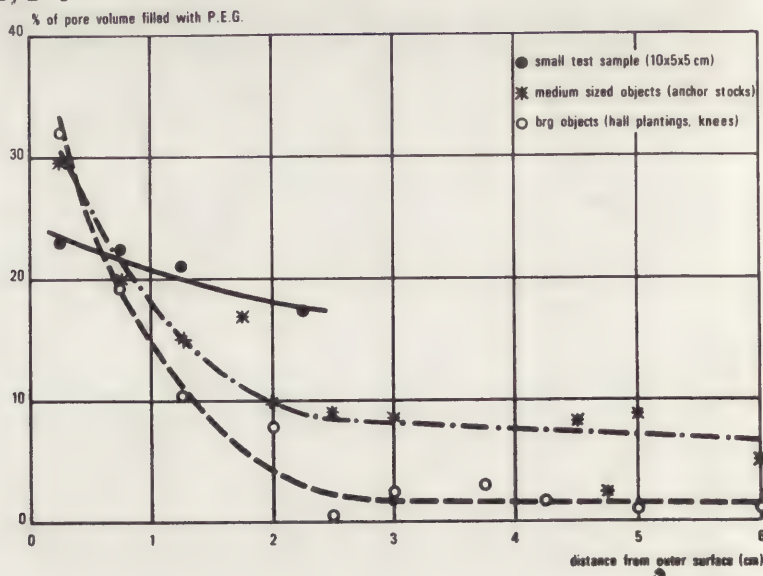


fig. 2. Impregnation results for small test samples, medium sized objects and big objects after the same treatment process. The percentage of the pore volume which has been filled with PEG is plotted against penetration depth.

be applied. In rare cases where these areas are comparatively small this general statement cannot be applied: for example a piece of planking consisting mainly of type 1 oak with a few minor cores consisting of type 2 (or 3), might be treated in a warm bath.

The final choice of the conservation method for the Zwammerdam en Utrecht ships was based on the following considerations. Due to the high degradation of the ships all have been salvaged in parts and sections which are permanently supported with boards of new timber. The biggest bottom plankings are about 4 m length, 0.7 width and 0.1 m thickness. The size of the objects to be conserved is well suited for a bath treatment.

Out of the methods described only for the PEG-bath method results of the conservation of rather big boats can be seen and judged. The PEG-bath process is a simple process which is rather easy to automatize. If based on an appropriate knowledge of the timber quality (watercontent as a measure for the degradation) satisfactory results can be expected. However timber of class 3 should not be exposed to a PEG-bath treatment. Hence all ships has been sampled following a regular sampling pattern for all major parts (ribs and planking).

This enabled the drawing of timber quality maps of the ships. Based on this information the decision with respect to the treatment to be given for any part of a ship can be made.

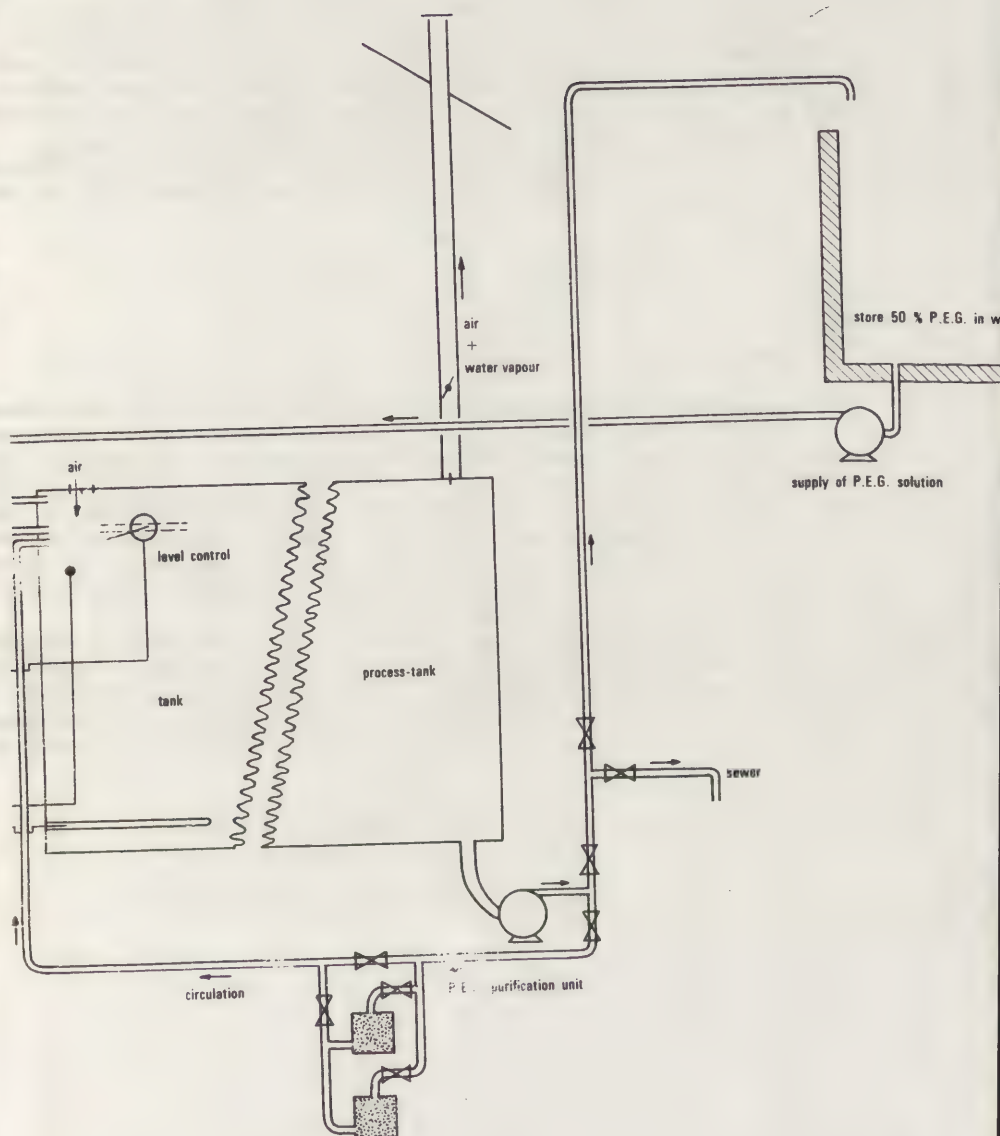


fig. 3. The process scheme for the automatized warm PEG treatment of waterlogged timber.

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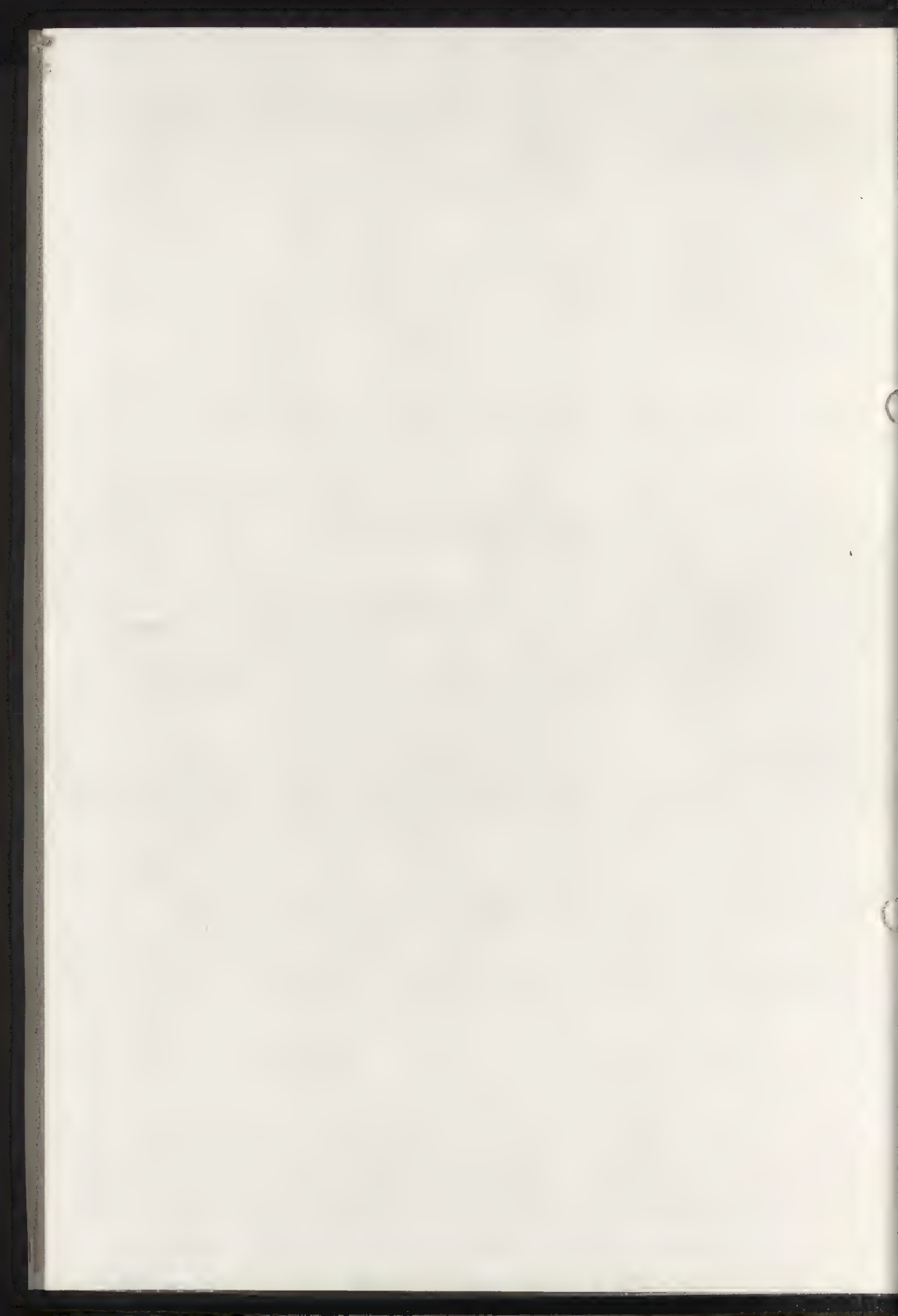
It was decided to start the conservation of the Zwammerdam en Utrecht ships with cold and warm baths of PEG 4000 solutions in water. The process should be highly automatized. The PEG should be purified constantly. Based on these requirements a PEG impregnation tank was designed. The scheme of the automatized warm PEG treatment process is given in fig. 3. PEG is introduced as a 50% solution by means of an adjustable pump. In order to increase the PEG concentration with time water is removed from the tank with the aid of an air current flowing over the water surface. If evaporation proceeds to fast water will be let into the tank. The water supply is operated through a level control unit. In order to keep the energy consumption during the conservation process as low as possible much attention has been paid to the thermal isolation of the tanks.

Summary

Since the IJsselmeerpolders Development Authority is among many other problems faced with the difficulties of the conservation of big waterlogged wood constructions (shipwrecks) an advising board of experts from Holland has been formed in January 1973. In that year also the Zwammerdam ships were excavated and it was decided that the conservation works should be done at Ketelhaven, so the board's first task was to decide what conservation process was most suited for these finds. After a study of several possibilities four methods were studied in detail.

Considerations pertaining to the quality of the wood of the Zwammerdam ships, the results already obtained by others, the possibility to automatize the process led to the conclusion that impregnation with polyethyleneglycol 4000 in baths offered the best opportunity if based on a detailed knowledge of the distribution of wood quality throughout the finds.

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LA CONSERVATION DES PALEOXYLES

Une méthode nouvelle de traitement physico-chimique des objets antiques en bois gorgé d'eau

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Nous avons déjà exposé le processus de dégradation subi par les objets antiques en bois ayant séjourné au fond de la mer ou des lacs, sous l'influence de micro-organismes déprédateurs qui ont consommé la plus grande partie des hémicelluloses hydrolisables.

Ce bois dégradé est donc devenu un matériau nouveau, dont la structure anatomique d'origine est à peu près conservée, mais dont la formule chimique est profondément modifiée. Pour le différencier des bois courants, nous désignons désormais ce matériau sous le nom de :

PALEOXYLE

(du grec palaïos=ancien et xylon=bois) lorsque plus de 10% du volume de l'objet a été dégradé.

L'expérience constante montre que tous les paléoxyles doivent subir un traitement dès la sortie de l'eau, et avant le moindre séchage, si on veut conserver leur structure, leurs formes et leur dimensions.

L'analyse chimique des paléoxyles révèle la disparition d'une importante quantité (pouvant atteindre 50%) de l'holocellulose globale, mais une bonne maintenance de la lignine, dont le taux apparent est beaucoup plus élevé que dans le bois. Cependant, le noircissement du tissu ligneux permet de supposer que cette lignine a subi quelques modifications. Mais surtout, on constate un accroissement important des matières minérales qui proviennent soit des substances dissoutes dans l'eau de mer, soit de la diffusion dans le paléoxyle d'éléments provenant du milieu dans lequel il a séjourné.

La fraction polyosidique qui subsiste est nettement enrichie en glucoses (galactose, mannose, arabinose, xylose, etc...) ce qui confirme que l'action du micro-organisme déprédateur était bien dirigée vers la création

des sucres nécessaires à son alimentation. Cette action a été sélective, puisqu'elle n'a pu s'appliquer qu'aux polyholosides susceptibles de s'hydrolyser naturellement en milieu marin. Elle a cessé avec la disparition complète de ces éléments qui ne représentent qu'une partie (30% à 40% suivant les essences d'arbres) de la cellulose du bois.

La richesse du paléoxyle en matières minérales dissoutes, ou en suspension dans l'eau qui l'imprègne, nous a conduit à penser qu'il serait possible de les précipiter "in situ" sur les parois des fibres qui subsistent par une réaction chimique. Ces précipités solides pourraient assurer une consolidation du parenchyme médullaire suffisante pour éviter, lors du séchage, les déformations habituelles des objets.

En nous inspirant des recherches fondamentales, entreprises depuis une trentaine d'années, sur la fixation dans le bois d'ions métalliques, nous avons procédé à des séries d'essais avec des solutions des sels des différents métaux (chrome, cuivre, arsenic,....etc.).

Les résultats ont été intéressants et, particulièrement, avec des solutions chromiques. Nous avons ainsi pu définir, empiriquement, un traitement qui provoque le durcissement recherché du paléoxyle et qui évite, pendant et après le séchage, toutes déformations anormales. Seul, un léger rétreint se produit, correspondant à la variation de volume existant entre un bois sec et un bois humide, et qui est toujours inférieure à 1%.

Après ce traitement, cependant, la dessiccation du paléoxyle est pratiquement totale, c'est à dire qu'il ne conserve pas les 15 à 18% d'eau qui subsistent dans les bois les plus secs. Cela provient du fait que cette eau de composition est retenue par le tissu intercellulaire, lequel est essentiellement constitué par les éléments les plus hydrolysables de la cellulose. Ce tissu a pratiquement disparu dans le paléoxyle. A sa place subsiste un certain "vide" interstitiel qui augmente la porosité, et, dans une certaine mesure, l'hétérogénéité du matériau.

On constate une égale dessiccation totale dans ce qui reste du paléoxyle non traité, lorsqu'il est devenu, après séchage, une masse informe et raccornie, et parfaitement anhydre !

Il est nécessaire de combler ce "vide" en bloquant dans les tissus ligneux une certaine humidité, sinon le paléoxyle traité restera très sensible aux variations d'hygrométrie, ou de température, du milieu dans lequel il sera conservé, et des tensions internes pourraient se produire, provoquant des ruptures ou, en surface, une fissuration en "peau de crocodile".

Le paléoxyle, fixé et consolidé par le traite-

ment aux sels de chrome, doit être protégé contre une telle éventualité, et nous avons obtenu ce résultat par un procédé, encore inédit, que nous décrivons plus loin.

TRAITEMENT de CONSERVATION

Le traitement complet du paléoxyle comprendra donc deux phases différentes.

Première phase - Le paléoxyle est plongé, tel qu'il sort de l'eau, dans une solution aqueuse de Bichromate de Soude ($\text{Cr}_2 \text{O}_7 \text{Na}_2$) et d'anhydride Chromique ($\text{Cr}_2 \text{O}_3$).

Par osmose, le paléoxyle va s'imprégner de cette solution, dans toutes les parties atteintes par l'eau de mer.

Le Bichromate de Soude réagit en présence des réducteurs organiques que sont les glucoses et donne un oxyde de chrome, qui précipite, en libérant du Sodium (Na). En s'hydrolysant, ce Sodium donne naissance à une soude (Na OH). Une deuxième réaction, plus complexe s'amorce alors : cette soude réagit avec l'acide chromique en présence d'un excès de Bichromate et donne naissance à des composés basiques qui précipitent des sels insolubles des acides organiques formés lors de la première oxydation. Les différents éléments minéraux présents dans le paléoxyle participent également à cette réaction en donnant des composés insolubles.

En fin de processus, la structure ligneuse est fixée par ces différents précipités minéraux qui se sont déposés sur ses fibres.

Le durcissement du paléoxyle peut être contrôlé pendant tout le traitement par des essais périodiques de pénétration d'une aiguille, à l'intérieur même du bain.

Lorsque le durcissement optimum est atteint, les objets en traitement sont retirés du bain et rincés, afin de délayer les excédents de sels de chrome, et séchés dans une enceinte close afin de ralentir l'évaporation. Le séchage est contrôlé par de fréquentes mesures de la variation pondérale. Il sera interrompu, à volonté, en engageant la deuxième phase du traitement.

On peut ainsi conserver, à l'intérieur du paléoxyle, une quantité d'eau correspondant à celle fixée normalement dans un bois sec de même essence, ou, éventuellement, en bloquer une quantité plus ou moins grande que la normale suivant que l'objet est destiné à être placé, muséographiquement, dans un milieu plus ou moins humide.

Deuxième phase - Le paléoxyle est un matériau poreux, mais les canaux qui permettent la circulation de la sève dans un bois vivant sont presque toujours oblitérés et,

chez les résineux, obstrués par la résine cristallisée. Il est donc pratiquement impossible de faire pénétrer assez profondément dans la masse des résines synthétiques condensables ou polymérisables, dont les molécules sont, d'une manière générale, plus grosses que les pores du paléoxyle.

Il est donc indispensable d'utiliser un produit très fluide, susceptible de pénétrer par effet de capillarité. Nous avons résolu ce problème en nous inspirant d'une idée du Professeur MONNIER, Directeur du laboratoire de Physiologie de l'Université "Paris VI", qui, pour les besoins de ses travaux, a réalisé des membranes extrêmement mince mais résistantes, par oxydation, sur une solution oxydante, de l'acide linoléique. C'est le phénomène de polymérisation oxydative des huiles dites "siccatives". Ces huiles sont des triglycérides formés par des acides gras non saturés. Sous l'effet de l'oxydation, les doubles liaisons des acides gras s'ouvrent et il y a combinaison entre des molécules distinctes ou de semblables doubles liaisons s'ouvrent également. Le processus aboutit à un réseau tridimensionnel d'autant plus aisément que les acides gras en présence possèdent un plus grand nombre de doubles liaisons.

Le paléoxyle, déjà traité comme nous l'avons indiqué plus haut, reste imprégné d'un excédent de Bichromate de Soude et d'anhydride Chromique, qui constituent un milieu très oxydant. En le plongeant dans un bain d'huile de lin, la plus courante des huiles "siccatives", cette huile va pénétrer par capillarité dans le parenchyme et occuper les "vides" intercellulaires laissés par la dégradation du tissu ligneux.

La polymérisation oxydative se produisant au contact des sels de Chrome, cette huile, très fluide au départ, va se transformer en une masse solide qui va, d'une part, consolider encore la structure anatomique du paléoxyle et, d'autre part, obturer définitivement les pores en emprisonnant les molécules d'eau qui subsistent puisque le séchage est incomplet.

Il est d'ailleurs possible que ces molécules d'eau se combinent avec des éléments libérés par la rupture des chaînes organiques de l'acide linoléique, en saturant les acides gras et en favorisant ou complétant la concrétisation de la masse. Des analyses, qui ne sont pas encore terminées à l'heure actuelle, permettront de préciser cette réaction secondaire. De toutes manières, nous avons constaté qu'un échantillon de paléoxyle "absorbe" l'huile de lin dans laquelle il est plongé pendant un temps très long, nettement supérieur à celui nécessaire pour la simple imprégnation par l'huile.

A titre indicatif : un échantillon de bois moderne, normalement séché, plongé dans l'huile de lin, absorbe environ 5% de son poids d'huile. Un échantillon de même volume d'un paléoxyle traité aux sels de chrome absorbe 15% (en poids) d'huile de lin. Dans les deux cas, évidemment, l'expérience a été poursuivie tant que l'absorption a été mesurable.

Lorsque le bois moderne est sorti du bain, l'huile était encore fluide et s'est polymérisé lentement au contact de l'air. Par contre, dans le paléoxyle traité, l'huile était déjà polymérisée et parfaitement concrète avant que l'échantillon ne soit remplacé dans l'air.

RESULTATS du TRAITEMENT

Depuis un an environ, nous avons multiplié les essais expérimentaux de ce traitement en deux phases, sur des échantillons de paléoxyle provenant de plusieurs épaves méditerranéennes. Dans tous les cas, le résultat a été satisfaisant.

L'objet traité conserve ses dimensions et ses formes, et la dureté du paléoxyle, après traitement est comparable (et parfois supérieure) à celle d'un bois moderne de même essence.

Le paléoxyle est parfaitement sec, il peut être usiné et collé avec les colles utilisées habituellement pour les bois de menuiserie.

L'objet traité est lavable, l'eau ne pénétrant pratiquement pas dans la masse ligneuse. Il est imputrescible, et, théoriquement, à l'abri des insectes xylophages (capricorne, lyctus, termites, etc.). Nous n'avons pas d'expérience suffisamment longue pour certifier ce caractère fongicide et insecticide, mais les composés chimiques présents dans le paléoxyle traité ne peuvent permettre la subsistance de ces insectes.

Enfin, le paléoxyle est devenu à peu près incombustible : la flamme d'un chalumeau le carbonise sans provoquer son inflammation.

Il faut toutefois noter une certaine limitation des caractéristiques physiques par rapport aux propriétés des bois modernes. L'élasticité a pratiquement disparu et la résilience est faible. On devra en tenir compte lors de la reconstitution d'un ensemble important, tel que la reconstitution d'une coque d'épave.

Cette méthode de traitement est relativement peu coûteuse. Elle ne met en oeuvre que des produits de classe industrielle et courants. La formule du bain chimique que nous employons actuellement dans la première phase du traitement est la suivante :

- 1000 gr d'eau ordinaire
- 250 gr de Bichromate de Soude
- 150 gr d'Anhydride Chromique

Cette solution est certainement surdosée, et nous étudions la possibilité soit d'une dilution plus grande dans l'eau, soit d'une régénération des solutions usées permettant de les utiliser pour plusieurs traitements successifs.

L'huile de lin employée est une huile courante, celle utilisée par les industries de la peinture. Cette huile sert pour plusieurs bains sans inconvénient.

Suivant la formule que nous venons d'indiquer, et aux conditions commerciales de 1975, le cout des produits consommables pour l'ensemble du traitement représente une valeur de 5 F par kilogramme de paléoxyle traité. Cette valeur paraît être un maximum susceptible d'être réduit après une plus longue expérimentation.

L'équipement indispensable est relativement simple. Il comporte essentiellement des bacs de dimensions adaptées aux objets à traiter. Ces bacs sont de simples cuves ouvertes (aucun dégagement de vapeur ou de gaz n'est à craindre), seulement dotées des canalisations nécessaires à leur remplissage et à leur vidange.

L'installation doit évidemment être complétée par les engins de levage et de manutention correspondant aux manipulations assez délicates des grosses pièces de paléoxyle avant traitement.

La durée totale du traitement varie avec les dimensions et l'état des objets que l'on veut traiter. Pour de petites pièces, elle est de l'ordre de 2 mois; Pour les grosses pièces, il faut prévoir environ 1 mois par centimètre d'épaisseur du paléoxyle.

Le traitement que nous venons d'exposer s'applique sans aucune difficulté particulière aux objets très dégradés, ou très attaqués par les tarets. Seules les manipulations avant traitement doivent tenir compte de la fragilité accrue du matériau.

L'expérimentation à grande échelle de cette méthode de traitement va être entreprise prochainement au Centre de Restauration des Objets de Fouilles Archéologiques de Marseille.

En effet, nous avons reçu une épave complète, datée du III^e siècle ap.J.C., qui a été remontée du fond de la mer dans l'Anse Gerbal à Port-Vendres, en 1974.

La coque subsiste sur une longueur de 13,90m. et sur une largeur de 7,50m.; elle comporte tous les éléments de la carène : quille, membrures, bordé,....etc. L'ensemble représente environ 15 Tonnes de paléoxyle qui sont, pour l'instant, placées dans un bassin d'eau de mer afin de ne pas sécher prématurément.

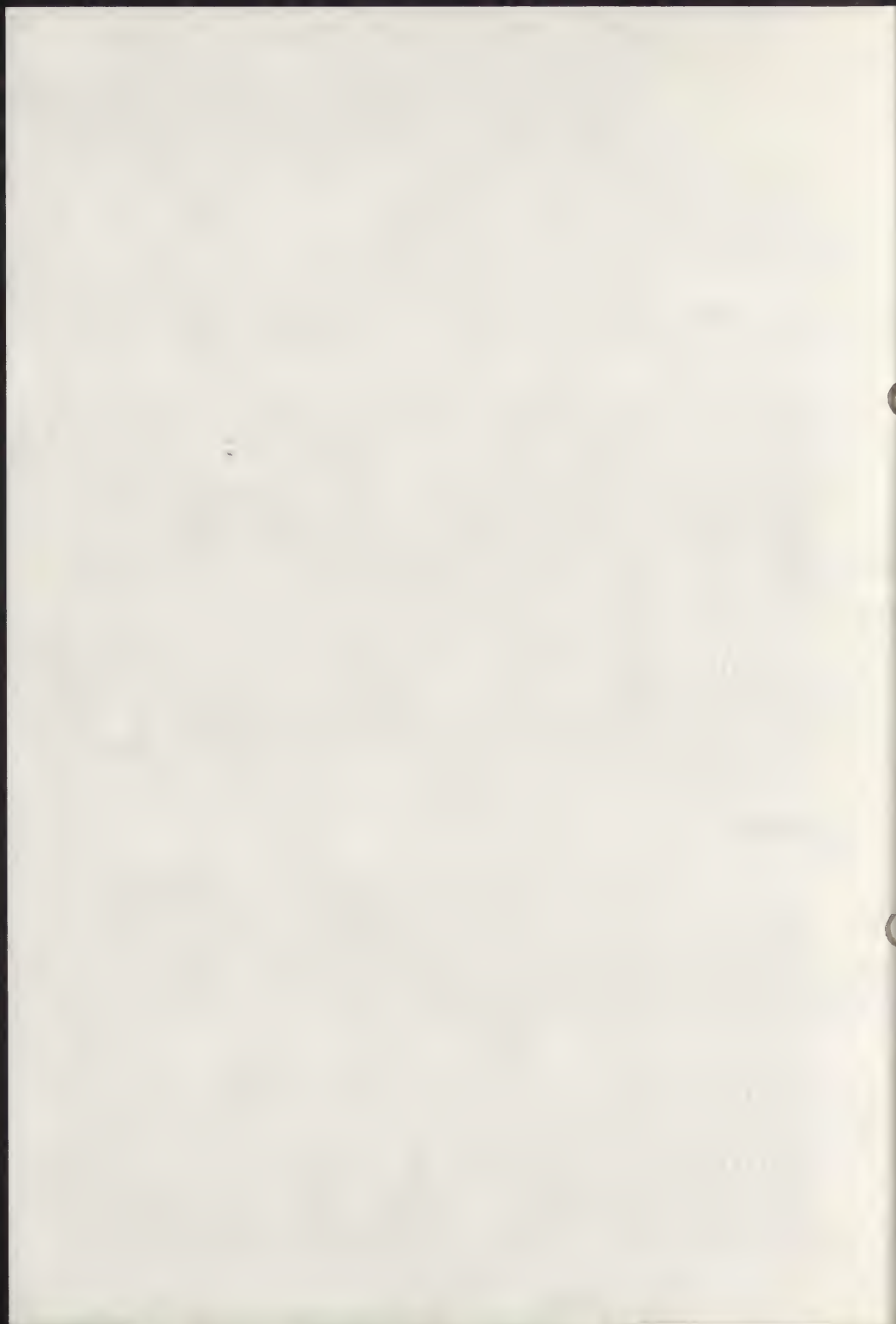
Dés que les équipements nécessaires pour traiter des pièces aussi importantes (certaines ont plus de 8m. de long, d'autres pèsent plus de 800 Kgs) seront réalisés, le traitement sera entrepris.

La conservation et la reconstitution d'une épave antique presque complète n'a, à notre connaissance, jamais été entreprise, et cette opération constitue une expérience qui permettra la mise au point définitive des techniques particulières d'utilisation de réactions qui, jusqu'à présent, n'ont été effectuées qu'en laboratoire. Nous pourrions ainsi vérifier si les résultats obtenus sur quelques dm³ de paléoxyle sont parfaitement valables, avec ou sans ajustement, pour des objets pesant plusieurs centaines de Kgs.

Plusieurs années seront nécessaires pour réaliser cette reconstitution. Une étude détaillée des travaux et des résultats sera publiée après son achèvement, mais, dès à présent, nous sommes à la disposition des chercheurs intéressés par notre méthode de traitement, qui désireraient des précisions sur ses différents aspects ou sur les techniques de mise en oeuvre.

RESUME :

La substance des bois antiques gorgés d'eau est tellement dégradée qu'elle constitue un nouveau matériau désigné par le néologisme : PALEOXYLE, afin de le différencier du bois normal. La nouvelle méthode de traitement comprend 2 phases successives : d'abord, une série de réactions chimiques qui précipitent dans la masse ligneuse des éléments insolubles solides, puis ensuite, une imprégnation avec de l'huile de lin qui durcit à l'intérieur du parenchyme par polymérisation oxydative. Le paleoxyle ainsi traité devient très dur, imputrescible et incombustible, mais les formes et dimensions de l'objet originel sont parfaitement conservées. Cette méthode ne nécessite que des équipements simples et faciles à réaliser. Elle est peu onéreuse. Une expérimentation de cette méthode va être entreprise sur une grande échelle : le traitement et la reconstitution d'une épave romaine complète.



CONSERVATION OF WOOD WHICH HAS STAYED IN WATER IN THE
P.R. OF BULGARIA

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During a period of ten years members of the staff of the Research Laboratory of the National Institute for Cultural Property have conserved a number of wooden objects, removed from sea or lake water, or, under the permanent level of subterranean waters.

But because of poor knowledge of archeologists of how wet wood should be stored until its conservation, quite often it entered the conservation process in a dry, or, semi-dry condition. Only in the past two years we have been informed in time for each interesting find. In these cases, naturally, the results were very good.

This paper includes conservation of: dry wood of absolute humidity below 22%; wood with humidity from 22% to 32%; wet wood from 32 to 80%, and very wet wood - above 80%.

For the stabilization of wood which has stayed in water, but of absolute humidity dropped below 22% (production and operation humidity) different methods are applied under which dry wood is conserved here.

Wood with humidity, ranging from 22% to 32% (within the limits of fibre saturation) no stabilization can be undertaken with resins and natural waxes, dissolved in oil solutions, as the latter cannot penetrate into comparatively wet medium. Therefore, they are treated in PEG solutions in ethyl alcohol, or, in a mixture with water by gradually replacing

it with ethyl alcohol. Thus PEG enters deeply, penetrating into the intermicelle cellular space and wood humidity drops under 22%. After achieving this low humidity, treatment begins in technology close to that which is employed for wood conservation with humidity under 22%.

Wood with humidity from 32 to 80% (approximately the maximum possible humidity of the nucleus, or, the ripe wood of various wood types) is soaked in water until full absorption. After increasing the moisture, conservation is performed after technology for wood conservation with moisture exceeding 80%.

Wood with humidity, exceeding 80% (approximately the maximum possible moisture of the nucleus, or, of the ripe wood) is conserved by increased PEG concentrations, dissolved in water, or, in water and ethyl alcohol by coating, spraying, or, immersing in water. The technology of wood conservation with humidity exceeding 80% by bath immersion is reported in the paper "Conservation of One-Log Boat" presented in Madrid in 1972 (4).

A. CONSERVATION OF DRY WOOD UNDER 22%

1. "RUDAN"

A "Rudan", made of oak tree (probably the 17th century) was removed from the seabed near Kaliakra. In the sea the wood had been attacked and destroyed about 60% by the ship worm (*Teredo navalis*) with channels of 2 - 3 mm. After the Rudan was taken out its wood received certain prism

tic cracks and splits (2,3).

After successful mechanical removal of the deposits and other foreign bodies, sticking out on the wood, it was processed in the following manner: a) the wood attacked by the worm was injected and washed well in 5, 10 and 3% PEG 4000 solutions in a dichlormethane and tetrachlormethane mixture, b) the wood, coated with rust was treated in 4% paralloyd B72 solution in toluene.

After stabilizing the wood, protective and anti-static treatment was performed with the following: 2 parts PEG, 2 parts cosmoloyd; 1 part pentachlorophenol and 95 volume parts turpentine.

On completion of all operation the wood acquired a fine appearance and good strength properties, approaching a healthy wood.

2. Conservation of a one-log boat near Burgas

The boat was found in the swamp near the village of Skala, (Burgas District) in 1968. Although, its condition was quite good at the time it was found, as later it was not placed under a special care and urgent conservation, it was completely destroyed in its superficial layers, at places strongly warped and with cracks.

After conducting some technological tests, the stabilization of the boat was made by 3,6,9,12,15 and 10 PEG 4000 solutions in a mixture of dichlorethane and tetrachlormethane, with temperature of the solutions ranging from 80 to 120°C. The superficial protection was made by smearing with a composition of: 3 parts Paraloyd B72; 2 parts Kosmoloyd and

95 volume parts of toluene. After the conservation the boat was exhibited at the local museum.

Inspite of the fact that the conservation of the wet wood should be carried out right at the moment of its taking out, our archeologists and others continue to ask for help with certain day, only when they establish that the work begins actually to be gradually destroyed. For this particular concept we think that the abovementioned technology of conserving wood which has dried up to a certain extent can find application.

Conservation of a knife from a sarcophagus from
Pliska

When the knife was taken out it was an amorphous mass. The water content of the wood was from 25 to 32%. Cleaning was effected by stabilizing the general mass by 5% Polyethylene glycol 4000 solution in ethanol and water in 1:1 ratio by adding 1% sodium pentachlorophenolate for disinfection. The mass was poured down and particles of earth and other additions were gradually separated. Photographic documentation was made after each major cleaning.

The process of driving the water out of the intermicelle space in the cells was done by periodical baths for 4 to 16 hours in polyethylene glycol in an increasing concentration of 6-8-10-12-16-20%. About 100 particles from the holder and the holster of the knife were separated and stored separately, when the general mass was cleaned. For the final driving out of the water from 12% upwards the polyethylene glycol was dissolved in ethanol alone.

The stabilization of the knife by polyethylene glycol continued about 3 months. When the water content of wood became within the limits of 7 and 9% additional increase of the artificial wax began in depth by 3% polyethylene glycol in ethanol solution treatment.

After drying (alcohol evaporation) additional stabilization by Paraloyd B72 solutions in toluene from 5 to 15% began as well as spraying the wood until absorption. The last spraying was made also by 3% solution and cleaning of shining was made by toluene. This stabilization process also lasted for about a month. Not only the knife's handle and holster were cleaned in the above-mentioned technique, but all the articles, found in the soil, were dusted off also. After this stabilization the holder(handle) had to be strengthened - it was bent about 40° to the central axis, beginning from the loop towards the end of the knife. Microscopic observations showed that the spring wood had been completely destroyed and the wooden mass was nearly divided in small prisms along the core rays and along the fibres. For that reason no bath stabilization was undertaken and it is impossible to place the whole stabilized holder in a solution to straighten the bend. The straightening was done by submerging the part of the bending in Becher dish, containing 10% Paraloyd B72 solution in toluene with the addition of 15% glycerine. Every 15 minutes a check-up was made to see if the mass is sufficiently soft to begin the straightening. After the holder was straightened, the loop and the metal parts at both ends of the holder were

removed also from the holder to make an analysis and conduct the conservation.

X-ray investigation was made at the beginning of the conservation to establish the place of every metal part to achieve better manipulation with them and the supplementary X-ray pictures of the holster together with the core by releasing X-ray of various length and intensity established that the iron has no core, but has been completely destroyed, being turned into a mixture of iron oxides (rust).

Therefore, it was impossible to remove the knife from its holster, as it was non-existent in fact. Then it was resorted to the simultaneous stabilization both of the rust and the wood, as it was mentioned above.

In order to obtain a dark colour the metal had to be smeared by a paste, containing orthophosphoric acid, methanol, graphite, and zinc oxide by multiple smearing. This treatment also has some protective functions with a view to the fast decomposition of the iron compounds. Protective treatment both of the wood and the knife was conducted after drying with Paraloyd and Cosmoloyd solution in toluene and turpentine for the wood, and toluene alone for the iron.

Before applying the protective treatment of the wood, each particle, already stabilized was located on the holster or the holder of the knife. At the final binding together of these particles it was established that the holster was protruding in its lower part by 45 mm, covering the internal

part of the knife holder; in that particular part the leather went round the knife, holding the holster and attached to the belt by the corresponding cord.

3. Conservation of a wooden coffin from a sarcophagus from a mound near Burgas

A burial mound was excavated near Burgas in June 1972 and the stone sarcophagus of a Thracian burial, dating back to the 2-3 century, was opened. The burial was carried out by laying the body in a wooden coffin of external dimensions 1900 x 570 mm (width at the head), or, 540 mm (width at the legs) x 410 mm height. The lid has not been preserved. The coffin had been seriously damaged in its base. The planks of which the sarcophagus has been made are 20 cm thick with a very well finished surface and shavings have been preserved from their planing, preserved together with the coffin.

The four outside angles of the coffin are secured together by grooves and teeth. In its upper part it is reinforced by metal clamps, sized 73 to 80 mm wide 2 x 55 mm and 5 mm thick.

Before conservation the coffin was cleaned up by water jet and brush scrubbing.

The water content of the wood was measured: it was 24,6%, or about the point of fibre saturation.

The six-month treatment of the coffin and the shavings was conducted by smearing it daily on several occasions by 5, 10, 15, 20 and 25% PEG 4000

solution with 1% of sodium pentachlorophenolate in water and ethanol in 2:1 weight parts. The following treatments were in 30,35 and 40% PEG water and ethanol solutions in 2:1 weight ratio until finally only ethanol was used as a solvent. At 35% - 1% of glycerine was added, each at 40% - 2%. With higher concentrations it was resorted more frequently to heating with ICL, until the complete penetration of the carboway, remaining on the surface.

With a view to the equal distribution of the PEG, the treatment was conducted by multiple smearing with 3% solution in ethanol by the addition of 1% glycerine.

Cleaning was effectuated by ethanol smearing, heating with ICL, or, blotting with a pad.

After a series of laboratory tests, it was established that Paraloyd B72 in 4 weight parts, Cosmolyd in 3 weight parts, and toluene in 93 volume parts, was the most suitable composition for protective treatment. This treatment was conducted by double smearing with the compound.

The coffin, conserved by the above described technique was a success. The previous deformations and cracks did not increase. The outside appearance was very good and the colour was preserved.

The coffin has been exhibited under ordinary conditions at the Burgas District Museum.

C. Conserving wood with water content from 32 to 80%

An interesting water collecting equipment was discovered in the town of Pernik in 1972 in which comparatively wet wooden parts were discovered (50 to

60% water content).

The parts were left in water for five days with a view to increase their water content to above 80%.

After cleaning the parts mechanically their stabilization treatment was attempted. It was conducted in a bath by the technology, described in Section "D", the initial concentration being just a little lower (5% - because of the lower water content of wood. As the sizes of the part were comparatively small, the conservation process was greatly reduced i.e. - 73 days. After that period, the parts were taken out, cleaned and rendered hydrophobic. After the conservation the parts preserved their volume and colour, increasing their brightness greatly.

D. Conservation of wood with water content above 80%

Conservation of a one-log boat from Varna

A one-log boat(4) 3150 mm long, 525 mm wide in the middle and about 350 mm high in that part was discovered in the Varna Lake in 1970.

After the boat was cleaned off there were traces indicating the manner of making the boat combined with burning.

The condition of the boat wood was very poor; it has been attacked by microorganisms and had very poor physio-mechanical qualities.

A number of laboratory and technological investigations were carried out, including: microbiological investigations; microscopic determination of the wood type (Querque fraineto Ten); a piece of it

was sent to the British Museum to determine the age of the boat by the C14 method; Brinell hardness test was also performed; absolute humidity of the boat wood (135 up to 142%), etc.

After cleaning the boat of deposits, it was placed in a bath with 7% PEG solution. The solution concentration and temperature were raised by a special regime (4,5) in the course of 475 days after which the solution was cooled to 45°C. The boat was removed by a special lifting equipment after which: the surface was cleaned off; protective treatment was conducted and the broken parts during their removal were replaced to their original places.

On completing the process of conservation the boat was exhibited under ordinary conditions in the first hall of the Varna Archeological Museum.

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A B S T R A C T

During a ten-year period collaborators of the Research Laboratory of the National Institute for Cultural Property have been conserving a number of wooden articles removed from sea or lake water, or under the permanent level of subterranean waters. According to the absolute wood humidity (dry - humidity below 22%; semi-dry - from 22 up to 32%; wet - from 32 to 80%, and very wet - above 80%), the conservation method is selected respectively.

For example in the case with "Rudan", found in the Black Sea, and the one-log boat, whose humidity was less than 22%, methods, under which dry wood is conserved, were applied.

The wooden coffin excavated near Bourgas, with a humidity 24,6% and the knife with wooden holder and holster from the coffin in the town of Pliska with humidity from 25 to 32% have been conserved with PEG dissolved in water and ethylalcohol, the water being continuously replaced by alcohol.

Parts of water-collecting equipment in the town of Pernik with humidity 50 to 62% were soaked in water until it became more than 80%. These parts were conserved in a bath with water solution of PEG by increasing the concentration from 7 to 90%.

A one-log boat found in the Varna lake with humidity from 135 to 142% was also conserved in a bath as stated above.

The results from conserving the above-mentioned articles are very good.

STABILIZING DEGRADED SWAMP WOOD BY FREEZE DRYING

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Abstract

The characteristic and irreversible damage which accompanies the unrestrained drying of water degraded wood has proved difficult to treat until the introduction of polyethylene glycol over fifteen years ago. The widespread acceptance of the total bulking and water replacement properties of polyethylene glycol has not always led to successful treatment of swamp wood. An alternative method of wood stabilization is available which is based on the removal of water in saturated wood by its sublimation as ice in vacuum or at atmospheric pressure. Vacuum freeze-drying has been successfully used as a standard treatment for wooden implements from excavations in Papua New Guinea, and in the treatment of 10,000 year old boomerangs from swamp deposits in South Australia.

Introduction

The disfiguring dimensional distortions which often accompany drying processes in wooden cultural materials has received attention from many researchers engaged in museum conservation. ICOM reports assembled in published and unpublished form attest to the concern of conservators for treating the entire range of cultural items in wood, whether these be as building materials, furniture, machines or implements. Dimensional stabilization of wood continues to be a difficult problem, even for sound, recently milled timbers; the difficulties are greatly compounded by time and the multitude of aggressive environments in which wooden artefacts are found.

The primary reason for wood collapse, whether in drying modern green or ancient water degraded samples, is the surface tension of the receding water boundary on the drying internal surfaces of wood. This paper is concerned with the drying and stabilization of saturated swamp degraded wooden implements from archaeological sites in Papua New Guinea up to two thousand years old (Golson *et al* 1967), and boomerangs from South Australia which are up to 10,000 years old and probably the oldest examples of this missile in the world (Luebbers 1975).

Dimensional Stabilization

In the Papua New Guinea Highlands horticulturalists have added weight and durability to their wooden digging implements by storing them for periods in the acid waters of swampy areas; this practice has only recently been abandoned with the change from traditional heavy wooden digging implements to imported steel spades. Some of the implements which are subsequently lost or abandoned in this fashion, have a potential for preservation for thousands of years. The dimensional preservation of wood in this condition is often near perfect and can be compared with objects in a permanent deep frozen condition such as those of tomb burials of Pazyryk (Rudenko 1970). While the exterior form of swamp interred wood may appear to be relatively unchanged, the effects of time, temperature, microorganisms and the chemistry of swamp waters will have produced irreversible changes to its internal structure.

A. Water Displacement Bulking

The problem of imparting dimensional stability in swamp-degraded wood has two aspects: firstly the removal of free water from the object without creating drying stresses and, secondly; the consolidation of the dried wood with a strengthening agent which may provide total or partial bulking.

The solutions to the two problems, of water removal and stabilization, have often been achieved together with a variety of materials which displace water and remain to effect stabilization in the dried wood. Of the many materials suggested for this purpose the earliest and longest used by conservators is probably potash alum, which was the standard displacement compound for over a century in Denmark. The description of the use of this and other methods using various natural and man-made resins is well known (Christensen 1970; Moncrief 1968; Mühlethaler 1965; Munnikendam 1973; Tomashevich 1969).

The use of liquid resins, which can simultaneously replace water and be polymerized to solids within the treated wood is an active area of research which has produced acceptable results on a small scale, and holds promise of being suitable for larger items (Munnikendam (1973).

The conventional means for dimensional stabilization of sound timbers also generally rely on the impregnation of bulking agents such as the man-made resins which may include formulations of acrylic, acrylonitrile, butadiene, furan type, isocyanate, methylmethacrylate, phenol formaldehyde, polyester,

styrene and vinyl.* Some of these have been experimentally used by conservators but none has yet been adopted to the same extent as has polyethylene glycol.

Polyethylene glycol bulking

Polyethylene glycol is probably the best known of the recent bulking agents being widely adopted by conservators for a range of spectacular archaeological remains such as the raised ships of Western Europe. However there are problems in the use of polyethylene glycol which relate to the difficulty of impregnating heavy molecular grades above 1000 into wood (Tarkow *et al* 1966; Christensen 1970) and the marked hygroscopicity of grades below 1000. The recommendation to use polyethylene glycol 1000 (Stamm 1970) is also accompanied by the advice to provide low humidity levels for storage of treated wood. Swamp-degraded wood may have lost a large proportion of its original woody material so that heavy bulking may lead to weeping of the polyethylene glycol 1000 if relative humidity rises above about 40% or if the storage temperature rises above about 30°C. The satisfactory results in using polyethylene glycol 4000 for small items such as those described by Organ (1959) are not always achieved on larger items either in total impregnation or in the appearance of the treated object. Apart from the poor penetration of polyethelene glycol 4000, mentioned above, there is considerable leaching of soluble matter from the wood being treated in hot baths of increasingly saturated polyethylene glycol. This is apparent from the dark brown colouration of excess liquid in the treatment tanks. Worse however is the disintegration of fine surface detail on badly degraded wood specimens. In any total bulking system the ratio of bulking agent to wood substance will increase as the degrade increases. With the polyethylene glycol treatment the more degraded the wood the larger the amount of polyethylene glycol present and the poorer will be the preservation of the artefact's surface appearance. The considerable solvent power of polyethylene glycol has been pointed out by Hey, Althöfer and Organ (1960) while it is itself unstable in the presence of phenols and tannic acid.

Recent work by Kreicuna and Svalbe (1972) reports on the damage to sound wood containing polyethylene glycol where pine sapwood had its hardness reduced by 10-13%, its tensile

* Up to date information on progress in the development of sound wood stabilization can be found in abstract form such as *Wood Industry Abstracts*, published by Washington State University Engineering Extension Services, Pullman, Washington; and *Forestry Abstracts*, published by the Commonwealth Agricultural Bureau, Farnham Royal, England.

strength reduced by 19%, and its compressive strength reduced by 16%. Of course these results have to be considered against the considerable advantage of polyethylene glycol as a very effective dimensional stabilization agent, particular for the treatment of sound wood (Stamm 1964:334, 1974; Pankevicius 1968). The impasse for the use of polyethylene glycol in degraded wood remains that, while the lower molecular weight grades, below 1000, are the most effective in producing dimensional stabilization, and are the only ones which can penetrate some larger specimens to sufficient depth, they have the distinct disadvantage of high hygroscopicity which makes them generally unsuitable, for museum conservation purposes, when they are used in heavy bulking concentrations.

B. Drying

The special problem of drying water degraded wood relates to the considerable amount of original woody material which may have been lost by solution and biological attack leaving the main structural component, cellulose, severely depleted. Water, in filling all the pores and voids in such wood prevents a general collapse of the structure by acting as a bulking agent. The degrade or depolymerisation of the cellulose chains reduces the coherence of the structure and produces a relatively disordered material which only maintains its shape while the bulking water is present. The surface tension force of water drying from wood with this weakened disordered structure can be completely destructive.

In order to avoid the surface tension damage various replacement liquids have been used which have a lower surface tension than water and are non-polar. These displace the water by its gradual dilution and in evaporating away themselves cause less shrinkage in the drying object. The most familiar procedure is the water-alcohol-ether displacement series (Christensen 1970:28). Another method which theoretically might be expected to produce no surface tension drying stress is the removal of moisture by ice sublimation from the frozen wood.

Freeze Drying

The theoretical basis for the transfer of water vapour from a frozen surface, the energy requirements and the practical limitations are outlined by Rowe (1964:141) and Rey (1964:23). There is no great difficulty in producing the conditions necessary for freeze-drying. *Firstly*, the water vapour pressure above an ice surface has to be lower than the saturation vapour pressure of the ice so that surface condensation does not occur; the greater the negative gradient of the water vapour pressure the more complete is

the removal of water vapour from the ice surface. Vacuum is normally used to produce the vapour pressure gradient but it is also possible to achieve this at atmospheric pressure if the air can be dried to a low water vapour content. The advantage of using vacuum is that water molecules may be removed by mass flow whereas at atmospheric pressure a slower diffusion process will operate. *Secondly*, heat must be supplied to the ice surface to replace the energy lost by the removal of water vapour. The heat used is equal to that which would be necessary to melt the ice and convert the liquid into vapour.

Freeze Drying of Swamp Degraded Wood

Sublimation drying of solidified frozen water degraded wood has been investigated by conservators (Christensen 1970:29; Organ 1959:100; Rosenqvist 1959:65), but the general results, whether based on simple ice sublimation under vacuum or the more elaborate exchange of water for trimethyl carbinol and its later sublimation, has not been satisfactory. During treatment and when the treated wood was exposed to air it inevitably developed cracks and checks. Though bulk water may be removed it is unlikely that the surface bound water, which is attached to the enormous internal surface area of any wood, is removed to any extent by freeze drying (Rey 1964:38) even under a high vacuum. The surface tension of the small amount of surface water which remains, and the condensation of additional moisture when the object is exposed to normal air, will cause contraction and damage to the weakened wood.

Although the experimental results of Rosenqvist were not completely successful they did encourage further work. There are two forms of damage which wood can suffer in simple freeze-drying. The first is caused by ice rupture when the 12% expansion of water occurs on freezing. The second is the contraction of wood components caused by surface bound water which remains after normal freeze drying. The characteristic shrinkage damage is a random surface cracking pattern caused by the equalised contraction of the large internal surface areas affected by bound water.

Though it is not possible to restrain the freezing expansion of water, it is possible to accommodate it if a material which shrinks on freezing can be added in solution. The liquid grade polyethylene glycol 400 has a freezing range which encompasses the freezing point of water and can produce a reduction in solution expansion on freezing.

A 10% solution of the low molecular weight polyethylene glycol 400 will separate on freezing into two phases of ice and wax with a reduction in total expansion to about 5% and conversion of the solid hard ice into a more pliant mixture of

microcrystalline water and wax. The grade name of the polyethylene glycols represents the average molecular weight which in the case of '400' spans a wider range. A proportion of polyethylene glycol will freeze at progressively lower temperatures so that the separation of ice will be occurring while some polyethylene glycol will remain liquid. The liquid fraction may migrate to lower pressure areas and so further accommodate the expanding ice crystals. If this frozen mass can be placed in a very low water vapour pressure environment the ice will be preferentially removed by sublimation while the frozen polyethylene glycol will remain as a porous structure. The very low vapour pressure of polyethylene glycol 400* of 9.0×10^{-5} Torr at 100°C , means that its evaporation rate is extremely low so that most will remain after freeze drying processing of a sample. Its porous structure would remain until it reached its melting temperature range when it would flow as a viscous liquid. In a degraded wood specimen the non-evaporating polyethylene glycol would replace much of the bound water and be further concentrated on the internal surfaces when it became mobile above its freezing range.

The surface tension of polyethylene glycol 400, 44 Dynes/cm, is lower than water, 72 Dynes/cm, and its presence on the internal surfaces contributes to the reduction in freeze-drying damage which normally follows from simple ice sublimation drying. The polyethylene glycols are structurally characterised by having two terminal hydroxyl groups. It is likely that these will form weak hydrogen bonds with degraded wood components and so counter the tendency for tensional collapse when free water is removed by sublimation.

The amount of polyethylene glycol necessary to treat an object in a case of complete bulking will be directly proportional to the sample's voids or its degree of degrade. In the case of freeze-drying the amount of polyethylene glycol necessary will be proportional to the internal surface area of the sample. Sound wood will have the greatest internal surface area to volume ratio, for as wood degrades, and cell walls and other structural elements are removed, the internal surface area is being reduced relative to the total wood volume. For freeze-drying purposes it could be expected that sound wood would be likely to require a greater concentration of polyethylene glycol, to satisfy its greater internal surface area, than is necessary for highly degraded wood. At the same time the total amount of internal surface bulking will only be a fraction of that necessary for total void

* Union Carbide, Carbowax 400.

bulking. The difference in the final concentration after treatment can be appreciated by comparing the ratio of dry woody material to polyethylene glycol in samples treated by total void bulking and by freeze-drying. A 100 gm sample of degraded wet wood which loses 80% of its wet weight on drying would, in total bulking, have only 20 gm of woody material to about 80 gm of polyethylene glycol. A freeze-dried 100 gm sample from a 10% polyethylene glycol solution would have 20 gm of wood material to about 7.5 gm of polyethylene glycol or less than one tenth that of the totally bulked sample.

An earlier report (Ambrose 1972) suggested a rather strict range of concentration according to the degrade of individual samples. Although it is generally true that highly degraded samples require less polyethylene glycol than sounder wood, the actual soaking concentration should be empirically adjusted according to the particular wood being treated. For most purpose a range between 8% and 15% has proved to be adequate.

The simplest method for determining the amount of degrade, in terms of a ratio of woody material to water at saturation, is to withdraw a small core of the wood with a sharp cork borer. This saturated sample can then be weighed before and after drying in order to calculate its water loss. Most of the Papua New Guinea wood ranges from fairly sound, <60% loss, to highly degraded, >75% weight loss. The least degraded specimen can then be separated for soaking in a higher concentration of polyethylene glycol from 12 to 15% while the most degraded can be soaked in a concentration between 8 to 10%.

The advantages of drying an object with a low concentration is that there is no danger of reducing the quality of the treated wood, either by disfiguring the surface or by being greatly altered by changes in storage environment. Additionally the treated object will be light and very porous so that further consolidation with more suitable materials is possible.

Application of Freeze-Drying to Archaeological Wood.

Wooden Spades

The freeze-drying procedures adopted for the treatment of wooden paddle shaped spades up to 3 m long have been described previously (Ambrose 1970; 1972). The archaeological project which has yielded large quantities of wood is continuing and further quantities of wood are awaiting treatment. The output of the plant is small at around 10 to 15 kg of wet wood per load. The drying time varies from a few days to a fortnight depending on the nature of the load, that is whether numerous small samples or fewer large items are

being processed. The greater exposed surface area of numerous small items will be processed faster than a load of fewer heavier items. Also, the cross section of the largest item will be the limiting factor in the treatment of a single load; this follows from the relationship of drying time to the square of the sample thickness (Rowe 1964: 155), but this relationship is likely to be modified by the geometry of the article being dried.

Boomerangs

A number of wooden items, including boomerangs, were uncovered in a South Australian swamp by careful excavation in 1974 (Luebberts 1975). The site had been used by hunters camped on the shore of marshy ground about 10,000 years ago. The condition of the boomerangs, and the associated digging sticks, was incredibly fragile and required special care in their recovery and transport. The degree of degrade which these materials have suffered can be seen from the fact that a 100 gm water saturated sample may contain only 11 gm of woody material on drying. This amounts to only one quarter of what might be expected in a sound sample of the same *Casuarina* wood.

The field treatment followed the conventional practice of removing the object with a surrounding matrix of peat. This was then contained in a close fitting wooden box with a screw fastened lid. For transport several such packages were placed in a water filled tub. At the laboratory the packages were carefully stripped of the enclosing peat and individual artefacts were placed in perforated aluminium trays together in shallow troughs. The soaking solution of polyethylene 400 at 7% concentration was kept at constant concentration at room temperature for at least six months. An antioxidant, Butylated Hydroxyanisole (May and Baker Embanox), and a fungicide, Sodium salicylanilide tetrahydrate (I.C.I. Shirilan), were added to the undiluted polyethylene glycol at .1% and .15% respectively before the soaking baths were prepared. The preliminary freeze-drying of the soaked samples indicated that a 7% solution of polyethylene glycol was insufficient and this was finally adjusted to 10% for a further three months before routine drying was begun.

Drying treatment

Each artefact was left in its metal tray for the entire drying process so as to avoid unnecessary handling damage.

- i A tray was removed from the soaking trough, drained of of all surplus solution and was placed in an insulated freezing trough.
- ii A sheet of aluminium foil was placed as a cover for each tray and the package was frozen in crushed dry ice for up to two hours.

- iii The tray was placed in the vacuum chamber on a supporting frame with thermocouples attached to the outer surface and interior of the thickest sample. Another thermocouple was attached to the supporting frame which also was later to supply heat to the drying samples (Figure 1).
- iv A rough vacuum around .4 Torr was used for most of the drying but this would reach .2 Torr when drying was complete.
- v Heat was supplied at about 35°C to 40°C to the metal trays and their contained artefacts after the operating vacuum had been achieved.
- vi During the process the temperature of the sample surface and interior, and the tray, were recorded as well as the vacuum. The refrigerated condenser on line between the vacuum chamber and the vacuum pump was kept at -40°C (Figure 2).

Results

The dried samples are very light and fragile but the finest surface finish and shape are well preserved. The colour is surprisingly like that of dried sound wood though untreated swamp samples dry with a characteristically shrivelled and dark brown leathery appearance. The boomerangs and other wooden materials were penetrated by the roots of swamp plants and are variously broken. A difficulty has arisen in assembling parts which are broken, for in order to record the shape and dimensions of the dried items some reassembly is needed. Ideally the various pieces should be consolidated before any attempt at reconstruction is made but their fragility makes this difficult. Further work in vapour deposition of polymerisable consolidants could be attempted on the very porous wood. Forming a more stable compound by reaction of the polyethylene glycol is an attractive possibility. Modification of polyethylene glycol in sound wood with isocyanates under vacuum has produced increased dimensional stability (Avella-Shaw 1974) and suggests an area of research which might be productive.

Radiocarbon dating In the same way as the treatment of the Papua New Guinea wood (Ambrose 1972:8), some concern was felt for the possibility of the polyethylene glycol contaminating wood which might be required later for radiocarbon dating. The boomerangs are sufficiently unique, at 10,000 years old, to warrant special care in verification of their age. Before any treatment on the wood was begun samples of peat from above the boomerangs were subject to soaking and treatment in the same way as were wood samples. A sample of polyethylene glycol with the antioxidant and fungicide additives was dated (ANU 1329) which produced a result with a slight activity above

75/8/4-10

background. The peat was divided into three samples (ANU 1344B1, B2, B3). B1 was dated without further treatment, B2 was dated with the polyethylene glycol present and B3 was dated after laboratory procedures to remove the impregnated polyethylene glycol. The polyethylene glycol impregnated sample B2 was apparently older because of the presence of the non-radioactive carbon (ANU 1329) in the resin. The untreated peat B1 and the purified sample B3 produced results which are indistinguishable. The result confirms that provided adequate decontamination procedures are undertaken, there is no problem for radiocarbon dating in treating samples with the drying procedures which have been adopted.*

Modified Freeze Drying

As mentioned previously it is possible to induce ice sublimation at atmospheric pressure and a small experimental unit has shown that it is possible to freeze dry swamp degraded wood in this manner (Figure 3). In this case the vapour pressure gradient was established by circulating dry cold air, at about 10 ppm moisture content, across the surface of a frozen wood sample held at about -4°C , which would have a vapour pressure producing an equilibrium moisture content of about 4000 ppm. Moisture should have no difficulty flowing down this concentration gradient and so reduce the water content of the wood by ice sublimation. Since heat flow through the drying shell is very rapid at atmospheric pressure the dried air was kept at around -3 to -4°C . A small sample was successfully dried in this way but the time taken to complete the operation was inordinately long requiring an estimated four times longer than processing under vacuum. The 33 gm wet sample with a 1 cm thickness required 6 days drying in the atmospheric pressure system but a similar sample could be expected to be dried in one to two days in the vacuum freeze drying equipment. The reason for the difference in processing time may be due to the difficulty of transporting water vapour through the drying shell; a slower diffusion process could be expected at atmospheric pressure compared with mass flow under vacuum. The results suggest that vacuum freeze-drying is more effective. An interesting study recently reported on the comparative speed of drying sound wood under vacuum and under heated kiln conditions (Choong *et al* 1973). The object of the study was to dry hardwoods without the destructive collapse which often occurred under kiln drying conditions. Apart from demonstrating the value of freeze-drying in avoiding this

* I wish to acknowledge the cooperation of Mr H. Polach of the A.N.U. Radiocarbon Laboratory for organising and working on this project.

damage, it was also shown that drying time was consistently less for vacuum freeze-dried than for kiln dried samples at atmospheric pressure.

Conclusion

Consistently good results in drying swamp wood can be achieved if careful field treatment is followed by vacuum freeze drying. The stabilized wood has a good appearance in terms of its fidelity to its original texture and colour. The highly porous and fragile nature of some specimens requires further work aimed at their consolidation.

* * * * *

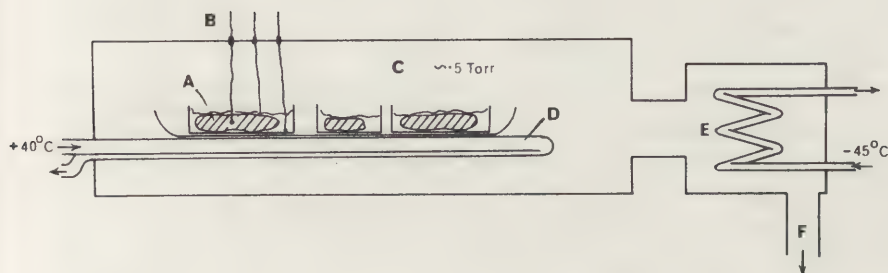


Figure 1

Schematic view of wood being freeze-dried under vacuum. The wooden boomerang pieces (A) are each contained in a moveable tray which rests on a heating plate. Thermocouples (B) are attached to the centre and outer surface of the largest sample and another monitors the temperature of the tray. The vacuum within the chamber (C) is kept at about .5 Torr for most of the process but will drop to around .2 Torr when drying is complete. Heat is supplied to the trays from a heating tube (D) which has a thermostatically controlled water pump attached and which operates at about 40°C. A cold trap (E) with coils supplied from a refrigerator at about -45°C ensures that no water vapour is carried over to the vacuum pump (F).

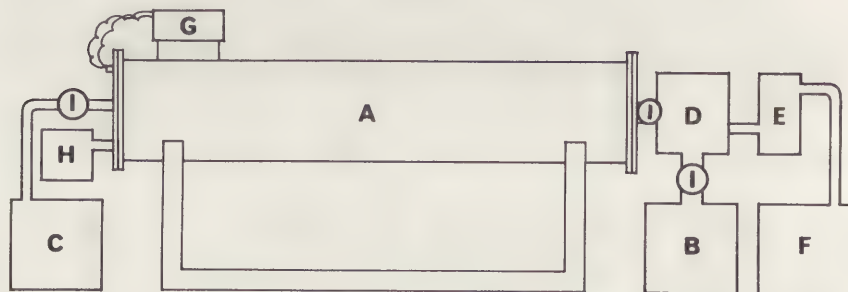


Figure 2 Schematic view of the freeze drying equipment. (A) The 30 cm diameter main vacuum chamber with one of the two 1.5 m sections in place. The end plates are fitted with standard 'O' ring vacuum seals. The main vacuum pump (B) which has a capacity of 300 litres per minute is a single stage gas ballast type capable of achieving .05 Torr. A smaller stand-by two stage pump (C) is operated when ice must be cleared from the condenser. The condenser (D) is a chamber fitted with a removable cooling coil which can trap 4 kg of ice before it requires emptying. The coolant for the coil is pumped from a reservoir (E) which has an alcohol coolant at -45°C . The reservoir is itself cooled by a mechanical refrigerator (F). A multiple input electronic thermometer and a vacuum gauge (G) register the temperature and pressure of the sample and chamber. Water from a thermostatically controlled tank (H) is pumped through heating coils within the vacuum chamber. Valves are placed to allow different sections of the system to be isolated(I).

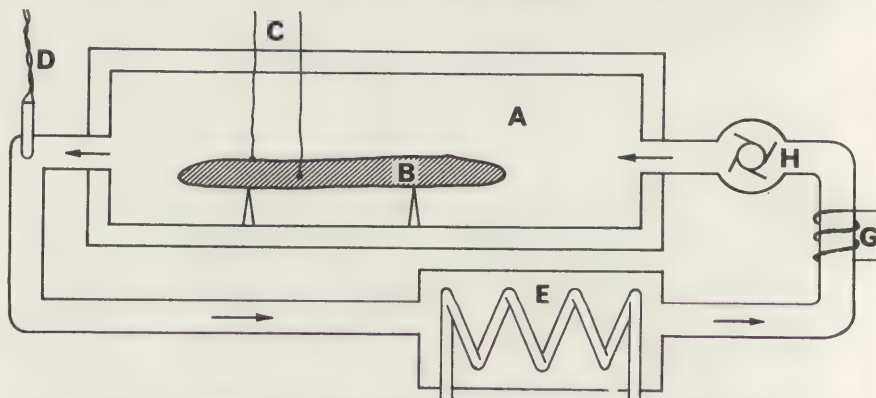


Figure 3 Schematic view of equipment for air-flow freeze-drying. The chamber of insulating material (A). The frozen wooden object is placed in the dry air stream to have maximum circulation across its surface. The temperature of the object is monitored with thermocouples (C). The moisture content of air leaving the chamber is measured with an electronic moisture sensor (D). A cold trap (E) supplied from a refrigerator dries the effluent air and cools it to -45°C . The dry cold air passes through a warming tube (G) and is impelled into the drying chamber at about -4°C by fan (H).

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CONSERVATION OF THE ARCHAEOLOGICAL WOOD WITH TRANSPARENT
SILICON ORGANIC POLYMERS

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Conservation of the organic materials found during the excavations is one of the most complicated problems of the restoration science, particularly for the wood found in the dry and moist cultural layer as well. Many attempts have been and are under taken to stabilize wood in our country and abroad.

Wood, as a product of the organic nature being in the earth is usually decomposed under the effect of the biological factors. However, in the individual cases despite its long existence in a strong dryness or moisture the wooden objects are still preserved. Wooden objects which were laying in damp swamps for a long period of time often preserved their shape and sizes, but serious changes lead to the loss of the artifact-strength. Wood which is excavated from the earth cracks at the drying. It is explained by the fact that gradual destruction of the cellulose components of the cell walls occurs as a result of the long stay in the earth and the mechanical strength of the wood decreases.

In the process of drying when water is left 25-30% the wood preserves its shape and the volume. At the further drying after this point which corresponds to the saturation point of the absorbed water considerable changes in the cell walls take place and cracks appear. When water evaporates the surface tension of the wooden substance affects weak cells which is often sufficient to cause the wood destruction. The content of the dry material in an old wood is less than a half of its content in a fresh one since the cells with the ageing lose a part of their cellulose. As a rule great changes are observed in old wood than in fresh one during drying process.

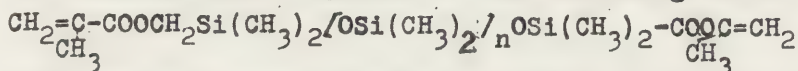
Prior to conservation the wood should be disinfected with antiseptics.

If the archeological wood becomes dark with time it can be bleached with 5% solution of hydrogen peroxide that allows to restore the natural colour of the wood. The problem of the wood strengthening includes two factors:

1. An active substitution of water without the wood structure destruction.
2. A content stabilization of dry wood.

We have designed a new method of archeological wood conservation. Polymerization of the liquid oligomer (i.e. polymer of the low number of polymerization chains) in the archeological wood pores is a basis of the suggested method. Since with the further oligomer polymerization in the wooden object pores setting is not almost observed, surface of the treated wood does not crack.

We have synthesized α, ω -di (metacrylate-methyl) - dimethylsiloxane oligomers of the following formula



with various number of siloxane chains ($n=12, 24, 53, 84, 160$). These oligomers are transparent liquids the mobility of which decreases with increase of the chain number. The permeability of these oligomers without the solvent in the archeological wood is high and the setting at the polymerization of the dimethylsiloxane oligomers with metacrylate groups takes place at 55°C . Benzoyl peroxide and CPC can be used as catalyst.

As a result of polymerization the transparent polymers are obtained. Polymer excesses may be easily removed from the surface of the wooden artifact after

impregnation.

The above properties of the polymers give a possibility of their use as a preserving material for the archeological wood. First we had tested the preserving property of dimethylsiloxane oligomers of the specimens of the archeological wood, i.e. an oak of the XVII c.B.C.

Cubes of various sizes were prepared out of the archeological wood for conservation and situated in closed vessels in which dimethylsiloxane oligomers were poured. Prior to this the catalysts were dissolved in oligomers. The wooden exhibits do not sink until the oligomer takes place of the water in the wood. Depending upon the size and the contact of the solid the exhibits lowered on the vessel bottom in 2 or 18 days. The impregnation of stronger wood, required more time. After the exhibits had lowered on the bottom the vessels with the specimens and oligomers were gradually heated. Benzoyl peroxide and CPC were used as catalysts. The catalyst was dissolved in oligomers by mixing. Only 0.2% of benzoyl peroxide were dissolved in oligomers with $n=12, 24, 86, 160$. CPC catalyst solubility in oligomers is high. The polymerization results at different amounts of catalysts are given in Table 2.

As the table shows the polymerization in the presence of CPC catalyst proceeds much quicker than with benzoyl peroxide. The polymerization speed increases with the increase of CPC amount. For the conservation of the exhibits oligomers with low number of links are more acceptable the best results were obtained with the use of oligomers with $n=12$ and 24. The polymerization of these oligomers in the wood at its

75/8/5-4

moisture of 26% in the presence of CPC catalyst, occurs in 1 hour. When the oligomer polymerization had ended the specimens were made free of excess of oligomers layer mechanically and dried at 35-40°C in two days and then at room temperature in 20 days. The air circulation can be increased by ventilation.

During the polymerization wooden specimens become dark, but after drying they obtained natural colour.

Cracks did not appear on the wooden specimen surface. The specimens completely preserved their shape.

TABLE 2

No of speci men	Number of oligo mer link	Amount of benzoyl oxide catalyst, %	Amount of CPC catalyst, %	Polymerization time
1	12	0.2	-	21h. 45min.
2	12	0.2	0.1	3h.
3	12	-	0.2	2h. 20min.
4	24	0.2	-	26h. 20min.
5	24	-	0.2	2h. 20min.
6	24	-	0.5	1h.
7	86	0.2	-	48h.
8	86	-	0.2	3h. 40min.
9	86	-	-	2h.
10	160	0.2	-	

The amount of the retained polymer in dried specimens was determined by weighing. As expected the polymer content in the specimens which contained more solid is less than that in soft wood.

The above specimens underwent the alternating

strong changes of humidity and temperature for checking the stability of the treated wood to the atmospheric effects.

The maximum temperature forearm ageing was taken as $45-50^{\circ}$. Six months artificial ageing showed satisfactory results.

Dimethylsiloxane oligomers with metacrylate groups at the ends are used as liquids with the following polymerization in the pores of the wood under strengthening. They have a series of advantages in comparison with known methods. The wood surface remains natural at the treatment by these oligomers. The colour of the wood does not change and the surface does not glitter. The specimen setting is almost not observed. The cracks on the wood do not appear. The treatment method is quite simple and requires little time.

We have treated the wooden funeral bed (barrow) found at the archeological excavation in Bediani, with the above mentioned α, ω -di-(metacrylatemethyl) dimethyl siloxane oligomer with the number of siloxane links $n=12$. The object results to the bronze epoch (23-21 c.B.C.). The exhibits fragments were preliminarily bleached using the method of Prof. E. Fogt. For this the carbonized fragments of the barrow were exposed in 5% solution of hydrogen oxide in two days and after ornaments appeared on the surface.

Then according to Kristenen method the wood was dried in several baths with ethyl alcohol with following immersion into ether baths.

After that the transparent liquid α, ω -di-(metacrylatemethyl) dimethylsiloxane oligomer synthesized by us with link number $n=12$ together with the catalyst was introduced. The ether was gradually evaporated

75/8/5-6

from the oligomer solution, in which the exhibit fragments (oak) were situated, by increasing the air circulation when ether had evaporated the pores of the archeological wood were filled with transparent oligomer together with CPC catalyst. Then the polymerization of these siloxane oligomers in the pores of the wooden object at 55°C was carried out according to the above method.

Generally the conservation of the archeological wood was done by the impregnation with polymer solution at the further solvent evaporation or by introducing the monomer into the wooden object pores and its polymerization at $65 - 95^{\circ}\text{C}$. In both cases a considerable setting is observed that is accompanying by cracking the wooden object surfaces. Besides, in most cases after treatment with various synthetic resins the wood becomes dark. In our cases at the polymerization of the siloxane oligomers the setting is very inconsiderable, due to which the cracks on the wood do not appear. The treated exhibits do not deform, their natural view and colour are preserved.

The carbonized nuts and chest nuts, the surface of which was covered with black amorphous layer due to the carbonization, were found in this grave.

The surface of this exhibits obtained its natural view after treatment with 5% solution of hydrogen peroxide. Then in order to strengthen them the surface of nuts was covered with the film of the dissolved silicon organic polymer by treating with benzene solution of the transparent silicon organic polymer.

Recently our laboratory got the historical documents of the wooden sticus - wooden charters (similar

to the birch bark charters found in Russia) of XIV - XV c., found in Svanetia in the altar of Saint Kviri-ke church. These charters represent the agreements between separate communities. The surface of the charters were covered with dense thick black layer of the century-old mud and dust under the church altar and in the wet earth. Inscriptions on some charters could not be seen. Some charters were strongly deformed and cracked as a result of the temperature variation.

The treatment of these charters has to be performed with care. First, the surface of the wooden charters is cleaned from the black layer in such way, that the inscriptions under this layer is not erased. Then these inscriptions and the wood are fixed simultaneously.

The black layer is removed from the charter surface with benzene and then with water vapour by means of a special vessel with glass tube. The inscriptions of the wooden charters appeared immediately. The charters were treated by gaseous insecticide as not to distort the inscriptions in order to protect them from the biological pests.

Then these wooden charters were treated by impregnation with benzene solution of the transparent cyclo-linear silicon organic polymer at the further evaporation of the solvent at room temperature.

After the treatment the inscription on the wooden charters became dark and all non-readable portions of the documents became readable.

The silicon organic polymer makes the wood mechanically strong and its steady film on the charter surface protects the inscription from the distorting effects of the atmosphere.

75/8/5-8

Hence, at the conservation of the historic exhibits of the organic origin with transparent silicon organic polymers of various structure good results were achieved and depending upon the type and the extent of the exhibits conservation the dissolving or non-dissolving silicon organic polymers of various structure can be used.

THE WORKING GROUP ON REFERENCE MATERIALS

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Abstract.

The intention of this paper is to stimulate discussion about future activities for the Working Group. Past activities, embodied in the reports of 1969 and 1972, are summarised. There are two aspects to the Group's activities: - publication and materials involved. The publication aspect has concerned: inventories of collections; information on acquisition; replication of photographic material. The materials aspect may be subdivided: specimens from objects; photographic records; specimens of known materials; analytical standards; ancient materials.

The last meeting of this Working Group was in Madrid on the 3rd October, 1972, with Mr. R. J. Gettens as Co-ordinator. Since that time, for reasons that will be touched on later, activity has lapsed. The purpose of this article is to review the field of "Reference Materials" as it exists in Museum Science and Conservation, to discuss what could and should be done, and to try to generate new ideas for further work. It is hoped that discussion will be stimulated during the meeting, and that members of the Committee will not hesitate to present their views. It is hardly necessary to add that the functioning of any Working Group depends on the existence of people prepared to play a constructive role. Without them, no Group can be viable.

A brief recapitulation of the Group's history may be useful. Undoubtedly, informal discussion among individuals long preceded any written propositions, but the first immediately relevant document appears to be a memorandum dated December, 1967, from R. J. Gettens to the Directory Board of the Committee for Conservation (1). It proposed the formation of a Working Group on Reference Materials, and suggested the following activities; (a) make and publish an inventory of cross sections and other slide mounts of samples from works

of art; (b) establish a depot for material accruing in Florence during work after the flood; (c) seek standards for ancient metal analysis; (d) collect material for use in training centres and in research.

The proposal was adopted with Gettens as Co-ordinator of the Group. In 1968 he sent out a questionnaire to many museum laboratory personnel; the results were analysed in a first report (2) presented to the Committee in Amsterdam, September, 1969. The questionnaire treated reference materials rather broadly, and distinguished the following: (a) samples, mounted or unmounted taken from artifacts; (b) materials of known composition and origin; (c) whole artifacts and fragments that may be used for experimental purposes, teaching, etc.; (d) radiographs, photomicrographs, photomacrographs, diffraction patterns, photographic or chart recordings from instrumental analysis. The response to this questionnaire indicated a widespread interest, and provided some basic data about things that are generally collected and their approximate numbers. Specific recommendations made in the report were: (a) continue to collect information on reference materials, particularly in smaller museums; (b) concentrate especially on collections of paint-layer cross sections and of radiographs; (c) seek ancient metal samples for analytical standards; (d) try to adopt a uniform method of classification, along with guidelines for storage and labelling; (e) try to establish a publication for these various data and other reference data.

This led to two further questionnaires being devised and circulated. S. Rees Jones investigated the distribution of X-radiographs and infrared photographs of (mainly) western paintings and published a tabulated inventory. M. Tabasso Laurenzi performed a similar task for mounted cross sections of paintings. These inventories appeared in the second report (3), presented at Madrid in 1972. Also presented at that meeting were a proposal from M. L. White (4) for replication and distribution centres for radiographs, information from R. L. Feller on sources and "banks" of bulk specimens such as pigments, and comments by Gettens on the importance of ancient objects themselves as "reference materials."

At the Madrid meeting Mr. Gettens, who had founded the Group and co-ordinated all of its activities, indicated that he wished to resign. This break, along with the fact that no specific recommendations for future work appear to have been generated in that meeting, has resulted in a period of dormancy. We are now faced with the question of what it should do in the future, and how best to generate useful activity.

From our point of view, there are two aspects to the Group's activities. Such activities have consisted, in fact, in publishing information about reference materials: where collections of them are to be found, how they can be obtained and so on. One aspect that we may consider, therefore, is that of publication: what it should concentrate on and how it can best be done. The other aspect is that of the materials: what they are, what is needed,

what is lacking and should be encouraged, etc.

I. Publication

The Reference Materials Working Group, more than some other Groups, is concerned to publish information that is simply not available elsewhere. Whereas accounts presented to other Groups of the Committee may often be incorporated later into a formal publication in one of the usual journals, inventories such as those of Professor Rees Jones or Mrs. Tabasso are available in the Committee's reports only. It follows that we have a special concern about the availability of reports. They can, I understand, be obtained in photoduplicated form from the Rome Centre (5); perhaps, however, we should pay some attention to seeing that persons coming new to the field, or those not previously concerned in the Committee's work, are aware of their existence, their contents, and how to procure them. This clearly infringes on matters outside the purview of this Working Group. Nevertheless, I think we may properly raise the question.

Publication has concerned a number of different efforts that fall into various categories.

A. Inventories of collections held by museums or individuals.

Two such inventories appeared in the 1972 report (3) and have been noted above. Possibly we should try to update these from time to time; it would be interesting to know people's feelings about this. Suggestions regarding other types of reference collection that might be the subject of international inventory would also be welcome. However, two kinds of difficulty have appeared with regard to this sort of work.

One problem is the large amount of work involved, not only by the person operating the survey, but also by the personnel of laboratories receiving a questionnaire. Where a large number of items is involved that have not been indexed in a form readily transferable to the questionnaire, it may be impracticable for the laboratory to answer questions in other than very general terms. This factor made it impossible for certain larger laboratories to reply to the cross section questionnaire of 1972, and it is a very real problem. Perhaps one should consider if there are alternative ways of gathering formation. Certainly, any questionnaire used needs designing with great care and with a full awareness of the problems created for the responder.

The second question is whether it is useful to create inventories of some materials at all. With regard to paintings cross sections, I have encountered sharply different views on the point. According to one view, a sample such as cross section forms part of the whole investigational record of the object concerned and would be largely meaningless seen in isolation. According to the other, the study of a related series of cross sections would itself yield useful information on, for example, trends in

technique; therefore it is useful to know where the sections are to be found. Perhaps further discussion is needed. Certainly, the task of the Working Group is to respond to real needs of those in museum laboratories and the identification of such needs is part of a rational scheme of work.

B. Information on the acquisition of reference materials.

By this is meant information on where one can obtain, by purchase or otherwise, analytical standards, identified specimens of pigments, dyes, fibres, wood species, or any of the multifarious things a laboratory may need as reference materials. R. L. Feller made a start in his 1972 presentation, with some sources for paper fibres, minerals, etc. I should hope to expand this part of the work. To do so successfully requires a "feedback" of information from other members of the Committee. There must be many sources, in different countries, which can supply material specimens, analytical standards or similar things. A classified list can be compiled, and could appear in the triennial reports of the Committee, thus being extended and updated every three years. Such a catalogue ought to be useful to many, and I should be pleased to receive suggestions of sources for reference materials, especially those outside the United States. In the meantime, attention is drawn to a recent publication on analytical reference samples in the earth sciences (6), and a less recent one on standards for spectrochemical analysis (7).

C. Reproduction of photographic material.

This is treated here as a particular case of publication. Photographs and radiographs are, to the museum scientist, "visual information," and the replication and distribution of them amounts to publication just as does printing and distributing verbal information. The case for lodging this function in specially created centres, at least for radiographs, was ably argued by Miss White in 1972 (4). There is now hope that such a venture will eventually go forward in the United States. A welcome development would be a similar venture in Europe, together with collaboration and exchange of material.

There may, of course, be a need for other kinds of photographic material. Examples are infrared photographs, photomicrographs and electron micrographs. One possibility would be to make these available from special centres, in the same way as with radiographs. Another would be to make the material available in conjunction with conventional publication.

Currently some scientific publishers, for example the American Chemical Society, offer "supplementary material" to certain of their papers. Commonly, this consists of long tables of numerical data which can be purchased as microfiche by those few specialists needing it; overloading of the printed version with data not needed by the majority is thus reduced. The question is whether some specialised photographic material could be treated in the same way. Where photomicrographs (for

example) are printed in periodicals such as Studies in Conservation, certain drawbacks are evident. Photographic quality is usually lost in the printing process, the size is limited, and colour reproduction, especially, is very expensive. While continuing to print halftone plates, the publishing house could, perhaps, offer as "supplementary material" photographic prints of micrographs, or other images, for a price that would cover adequately the cost of making them. Those few professionals who really need the extra detail and fidelity of a print would be able to get it. For most readers the printed plate would be satisfactory. Such a procedure might be one way of dealing with the problem of an image that carries additional information in its colour, but where the high cost makes conventional colour reproduction impractical.

II. Materials

Although it is not currently part of the function of the ICOM Committee for Conservation itself to form collections of materials, one may comment on what should be regarded as reference materials, how they may be classified, where needs exist that are not being met and so on.

A. Specimens taken from objects during examination.

Clearly, specimens of this nature are continually being obtained in laboratories; some are mounted for microscopic examination, some not. The question of making inventories of such things is dealt with above. There is little the Working Group can (or should) do to influence what specimens are obtained, though one might discuss what investigators should be expected to save for posterity, as well as the question of possible exchanges.

B. Photographic and similar records.

Collections of radiographs, photomicrographs and so on that relate to objects are subject to much the same comments as are object samples.

C. Specimens of known materials.

These have been accumulated in, for example, pigment banks (mentioned by R. L. Feller in 1972 (3)) and other specialised collections. The Working Group should be able to do several things, among them: (i) specifying what is needed before a specimen may be called a "reference material," (ii) identifying sources of supply and gaps in availability, and suggesting how the latter might be filled; (iii) dealing with questions of terminology.

(i) Specification. It is possible for collections of "reference materials" to be accumulated rather uncritically. Perhaps it is not enough to have a specimen of something in a vial, labelled with an ill-defined name that, one hopes, bears some relation to the contents. Rather one may look to materials that are quite fully specified: one may need to know not merely a common name for a specimen, but such details as where it came from and when, how and from what raw materials it was manufactured (in appropriate cases), various relevant

characteristics of the substance and so on. An example in this direction was the acquisition and distribution in 1972 by the Conservation Center of New York University of a collection of pigments from the National Bureau of Standards, along with data sheets on each. Another is the collection at the Mellon Institute of samples of lead white manufactured by various known methods.

I conclude that a valid task for the Working Group would be the specification of what is needed in a reference material. What do we need to know about pigments for samples of them to be useful in museum work? What about fibres, or samples of wood? Can we really write down a specification for a reference material in any given field?

(ii) Availability. This follows naturally upon specification; having decided what is required, one may face the question of how to obtain it. The publication of a list of commercial sources has been dealt with above. Gaps in availability may sometimes only be filled by an interested research worker making or acquiring his own reference materials for a particular purpose. Here, one can encourage the idea of making the resulting material available to other laboratories, perhaps by exchange. Again, a knowledge of what is required, and what materials are lacking, might be a useful first step.

(iii) Terminology. I do not know to what extent there are difficulties when we try to define precisely reference materials of any class in several different languages, but the problem should perhaps receive mention. If there is any question as to the relationship between ostensibly synonymous terms in various languages, then ICOM is surely the place to discuss it, to identify differences of usage and if possible to resolve them.

D. Analytical standards.

In museum and archaeological science, much interest has centred around analysis of metals. We recall the Program for the Comparative Analysis of Bronzes, conducted in the Working Group on Metals, and presented at the 1972 meeting (8). This was based on the analysis, by various laboratories, of two samples of ancient bronze. The variations in their results emphasised the uncertainties that abound when trying to compare analytical results of similar materials by different analysts. Since, nonetheless, such comparison often has to be made, we have to consider how to make it as meaningful as possible. This will require agreement on methods and procedures, a subject that falls more properly into Working Groups on appropriate materials. Agreement on the standard analytical materials to be used, which has already been urged (8), may reasonably be considered by this Working Group.

As a personal viewpoint, I would express scepticism about using ancient materials as working standards, at least in the field of metal analysis. In my opinion, correctly synthesised standards would be better, though ancient materials would be quite satisfactory for a finite project such as the Comparative Analysis

Program. My reasons for doubting the usefulness of ancient metals as working standards are as follows.

- (i) The difficulty of persuading those responsible to part with metal objects to be destroyed for this purpose. If this is a problem with bronze, how much more so with silver or gold!
- (ii) It is impossible to arrange in advance for elements to be present in ideal proportions for the purpose at hand. For example, neither ancient sample distributed in the Comparative Analysis Program contained enough lead.
- (iii) The quantity of ancient sample is finite. Sooner or later, it will all be used up, necessitating a completely new standard, and bringing one back to problems (i) and (ii).

I believe that an appropriate task at this stage is to specify ideal sets of primary analytical standards for particular purposes, and to seek agreement on their use. I am unaware of any attempt to suggest optimum elemental ratios, or physical form, for analytical standards applied to archaeological metal analysis. A range of standards may be required, even for bronze alone. Perhaps those intended for main element analysis will be different from those for trace element analysis. The first thing, in any case, is agreement on specification.

Agreed standards may or may not be commercially available. If not, one of the larger laboratories could perhaps undertake the task of making suitable alloys. An alternative might be to seek funding to enable this to be done commercially. Whichever way forward is chosen, there will be problems, but it seems to be agreed that quantitative analysis badly needs rationalising in order to facilitate comparison of results; of necessity, therefore, the problems must be tackled.

E. Ancient materials.

These have been taken to comprise either fragments of artifacts, or whole artifacts in such bad repair as to be of little interest for other purposes. One can conceive of "reference materials" that need to be ancient by the nature of their purpose. Certain dating techniques may require old material of known age for checking, normalisation or calibration purposes. For example, thermoluminescent dating of pottery has used archaeologically dated potsherds in such ways. The Committee for Conservation has not, so far, taken part in the selection and distribution of such materials; perhaps there is an opening here for consideration.

Other examples that have been discussed in this category may be more accurately described as "study materials," being suitable for individual research projects rather than forming agreed points of reference among different workers. This need not rule out incorporation of such materials in the purview of the Group if a valid purpose of international co-operation can thereby be served. The function of ICOM here may be to encourage the flow of information about materials available, and perhaps to facilitate their exchange.

Conclusion.

The foregoing discussion attempts to summarise work on reference materials both in terms of what has happened previously and what seems to be relevant now. It does not pretend to exhaust all possibilities, and constructive suggestions and criticism would be more than welcome. To refer back to an initial comment, the functioning of a Working Group depends upon people who will play a constructive role within it.

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METHODS OF REPRODUCING RADIOGRAPHS

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The available methods of copying radiographs may be divided according to the size of the resultant reproduction. The methods break down into three major categories: exact one to one direct copies; reduced formats approximately 100mm x 100mm; and microforms. I would like to discuss what these systems are and the relative merits of each in respect to cost, ease of copying, the quality of the final product, and the ease of use for a wide audience.

Direct 1:1 copy film has been available for several years. The film is exposed with a strong light source and then developed in standard x-ray developer. Litton Industries makes a Blu-Ray Mark II Radiography Duplicating Printer which copies a radiograph in six seconds on either Kodak RP/DX-MAT radiographic duplicating film, or DuPont duplicating film. The machine costs \$600.00. 14" x 17" Kodak RP/D film is \$72.95 for a box of 50 sheets. Dupont Duplicating Film is \$145.80 per box of 100 sheets. The film produces maximum upper scale contrast and density. It is also possible to vary the contrast of the original radiograph by changing the illuminant in the Blu-Ray Mark II.

This is an expensive method of copying both from the point of view of cost of materials and operator time, but it gives excellent results. It should be considered in those cases where one needs full size radiographs of only a limited number of objects in a collection. The great cost of copying as well as the amount of filing space required for such a system would not make it practical for an archival system.

Another method of copying radiographs should be mentioned as it is the one used by most museums at present. Direct photography of the radiograph on a light box to produce a negative from which a paper positive is then made is the most prevalent method of reproducing fine arts radiographs now. Anyone who has used this system knows how time consuming and unsatisfactory the results usually are. The soft print loses a great deal of definition which is recorded in the radiograph but gets lost in the printing process. If one has no other means of copying available then this method can be used as a last resort but it is totally unsatisfactory for an archival system.

There are currently two firms marketing reduced format copiers. LogEtronics, Inc., Springfield, Virginia and Old Delft Corporation, Fairfax, Virginia. LogEtronics' system consists of a radiographic reducer which produces a 4 x 5 inch negative or "black bone" from which directly viewable film prints, paper prints or 35mm transparencies may be made. The LogEscan uses a cathode-ray tube as a light source. The tube operates with a scanning photo multiplier which determines the correct exposure for each part of the film. The exposure can be controlled to enhance the contrast in the original image if it is too light or too dark.

The fully automatic LogEscan radiographic reducer Model RS-46 costs \$50,000 and can handle up to 100,000 x-rays in seven hours. The machine uses professional copy film. The intermediate or "black bone" negative costs 11 cents and each film transparency is 7 cents. The paper prints are 5 cents each. The LogEscan Model R-45 costs \$12,900. It is a non-automatic copier. The LogEfax stabilization printer/processor Model P-8 is \$345.00.

The advantage of the LogEscan system is that its "black bone" intermediary negative allows one the choice of making either transparencies or "white bone" prints as well as 35mm slides for projection if needed for teaching or other slide presentations. The 4 x 5 format is easily readable without magnification and provides excellent resolution from the original radiograph. The films cannot capture all of the contrast available in an industrial x-ray film, but they do retain all the available information of the original in a compressed contrast scale. This size may be viewed directly on a standard light box and makes comparison with other films very easy. They take much less storage space than conventional 14 x 17 inch films yet are easily retrievable.

Old Delft Corporation of America makes a 100mm x 100mm format direct copy processor which produces the smaller replicas without an intermediate step. The Delcomat copier costs \$17,500. and The Delcomat processor is \$21,800. The film used is either Agfa Geveart (50 sheets per box \$7.00) or Kodak RP (100 sheets per box \$20.00). The process is totally automatic and no intermediary step is required. Copies may be made from the 100mm duplicate with no problem. This is the most direct copying system. The initial production of as many duplicates as wanted is made just by setting the desired number of copies at the time the original is first copied. Thereafter one of the copies can always be used to produce another duplicate. The only limitation is that the system produces only the 100mm x 100mm format.

The 3M Company makes a positive-negative camera which uses a 35mm format. A new camera costs \$13,000; a used one is \$10,000. The film comes out as a film chip mounted on a regular IBM card. The film is made to record the density of medical scale x-ray film so misses the top end of the industrial film density. The film is very slow and takes about 6 to 8 seconds to expose.

Kodak now makes a 35 mm direct copy film Kodak SO-185. Radiographs are mounted on a standard light box and then exposures are made from them. The film is very slow with people reporting exposure times of 36 to 72 seconds at f3.5. The film is then developed in regular x-ray developer solution. The film costs \$3.00 per roll of 36 exposures.

The major drawback of the 35mm or other microforms format is that one must have a machine to magnify the prints. This makes comparison of a number of films very difficult. It also limits the use of the files to only those institutions which have a microfilm reader. Thus a scholar could not take a whole set of one artist's work to study in his office or home unless he had some means of enlarging the film chips. Great care must be taken in film handling on a micro scale so no dirt or scratches get on the film chips. Even a slight scratch can irreparably mar a film.

The resolution is excellent in all of the above systems. Currently none of the films used for copying will capture the full range of contrast available in industrial x-ray film as they are all made for copying medical radiographs. However, the films will record everything that is visible to the eye on an ordinary light box. Thus the films miss only the dark areas which are brought out with a high intensity illuminator.

If an international reference center is to be established, and I certainly urge that such a center for exchange of this information be made available, then a uniform method of copying must also be decided upon.

My preference at the moment is for a main center using either the 100mm x 100mm format or the 4 x 5 format, as these provide a working copy which can be viewed without the aid of magnification thus allowing individuals without viewing facilities access to this information too. If a system which produced a "master" negative is used then one always has the option of making a copy any size he wants just through photographic enlargement or reduction at a subsequent date. These systems also provide the quickest and easiest way of copying radiographs which is of prime importance when doing entire collections. The cost per copy for a secondary center or individual wanting a copy would be about 20 to 25 cents per copy which is not too expensive when one considers the high quality of the copy as well as the convenient workable size.

Abstract At the 1972 ICOM Committee for Conservation Meeting in Madrid, a proposal for the Establishment of Fine Arts Radiograph Centers was presented. This paper deals with the various methods which are now available for the copying of radiographs and compares the cost, ease of handling, quality of final product, and the ease of use for the various formats.

PROPOSAL FOR A REPOSITORY FOR THE MATERIALS OF BOOK
AND PAPER CONSERVATION

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ABSTRACT

A proposal is made for the collection and characterization of materials and test samples associated with book and paper conservation. The history of earlier, less ambitious, sampling programs is used to demonstrate the need for and benefits of a more broadly conceived program. The types of samples to be collected and the suite of test and evaluative procedures to be applied is considered. The role of manufacturers' data-specification sheets and conservators' treatment reports as supplements to the published literature is discussed.

INTRODUCTION

Technological advances, particularly in polymer science, have had an enormous impact on the techniques of artists and conservators. Both groups have an ever expanding range of options based on a wider group of available materials. With these options arises the responsibility to choose materials according to rational criteria. Polymer and cellulose chemistry provided us not only with a huge array of materials but also with a spectrum of working properties which makes the collection, codification, cataloging, and continuous monitoring of both new and old formulations absolutely essential for the ethical continuation of conservatorial praxis.

Similarly, a critical need exists for a collection of naturally aged and preserved artists', printers', and conservators' materials. Well characterized

samples, naturally aged under controlled conditions and samples preserved by storage at low temperature under an inert atmosphere will be of inestimable value to future generations of conservators, scientists, and historians.

While the need for a continuous cataloging of new materials is apparent from the sheer number of new substances, products, and formulations, the process of cataloging itself brings up problems worthy of careful scrutiny. Methods of testing and evaluation advance with technological developments and must continue to do so in order to describe as quantitatively as possible new properties and new formulations. It is important to establish a series of reliable, responsible test methods that can encompass the spectrum of properties characteristic of the materials of paper conservation. It is also important that the test procedures remain sufficiently flexible in their application to accommodate both new materials and new test methods as they appear.

Another important function for the repository here proposed is as a library: 1) of technical information obtained from manufacturers and private conservators; 2) of analyses independently obtained; 3) of conservators' observations of working properties collected under conditions reflecting actual experience with the material; and 4) of citations of materials used solicited from artists and publishers.

The continuous orderly collection and monitoring of materials under controlled conditions of natural aging would be an invaluable asset to the researcher. In a recent study (2) which attempted to evaluate the efficacy of a dip-impregnation method for the routine conservation of deteriorating old books, the authors were able to employ dated 19th and early 20th century books. It was possible to compare qualitatively test results on these naturally aged books with papers artificially aged. The limitations of such comparisons quickly became apparent to the thoughtful researcher. There was no clear record of the history of the naturally aged paper; the naturally aged paper itself was exceedingly non-uniform. A bank of naturally aged samples would provide an invaluable resource for comparative study. Not only would it be possible to follow the course of natural aging under carefully controlled conditions but the processes and correlations between natural and artificial aging of study materials would have increased likelihood of definitive description. The conservator would have available small samples of obsolete materials used by a previous generation.

EARLIER SAMPLE REPOSITORIES

Perhaps the most familiar case of sample collection and study over an extended period of time has been the program at the Fogg Museum (1). In 1938, 31 different surface coatings were painted out on test panels.

Twenty-five of these were fully characterized while six were proprietary coatings not identified by the manufacturers. The coatings have been examined on six occasions (1940, 1948, 1949, twice in 1961, and 1969) where solubility in five solvents, appearance, and related properties were observed. Though the results are of continuing importance in the study of varnishes, unfortunately, new materials have not been added to the study routinely.

A most unfortunate loss was the group of 72 book papers made in the National Bureau of Standards mill in 1937. These were tested before and after accelerated aging for 72 hours at 100°C (3). Since no plan to retain these samples for retesting at a later time was developed, sufficient samples remained in 1974 for testing only 18 of the original group.

In the same laboratory, a group of commercial papers was assembled and tested before and after accelerated aging in 1929. These were tested again in 1933, 1937, 1951, and 1955. These samples were discarded several years ago (3).

These few remnants have been of great value in work on the comparison of natural to accelerated aging and have assisted in the development of accelerated aging criteria.

The Forbes Pigment Collection provides an important source of comparative materials for those engaged in the study of pigments. For example, the obsolete pigment, Indian yellow, is represented by several specimens in the collection (4). The samples suffer from poor characterization. Many are certainly mislabelled.

THE PROPOSED SAMPLE REPOSITORY

Materials. Among the materials to be cataloged and stored are:

1. Adhesives
2. Fixatives and Coatings
3. Impregnating Agents and Sizing Materials
4. Media
5. Buffering and Deacidification Materials
6. Bleaching Agents and Samples of Bleached Papers
7. Pigments, Inks, and Dyes
8. Papers - treated and untreated
9. Leathers and Leather Preservatives
10. Where appropriate, treated samples, e.g., buffered aged and unaged papers, bleached papers, treated leathers, would be prepared under controlled conditions and added to the collection.

The first three of these materials are largely based on polymer technology and represents the most rapidly changing set of possibilities. Maintaining exhaustive and up-to-date information and samples on new materials would require careful vigilance. Sample storage would be regulated and continuously monitored with respect to temperature, humidity, light, etc. The shelf-life of the materials would be an extremely important property observed.

Testing and Evaluation. Some of the test results that would be recorded are:

1. Accelerated Aging Effects (variables: time, temperature, humidity, light, atmosphere, etc.)
2. Reversibility (Solubility in various solvents)
3. pH (surface, extraction) and reserve alkalinity (by titration)
4. Optical properties (objective color, reflectance spectrum, infrared spectra, scanning electron photomicrographs)
5. Mechanical properties (break strength, fold endurance, tear strength, tensile-stress relaxation-data)
6. Viscosity
7. Differential Thermal Analytic data

Tests and evaluations would be performed on the individual materials as well as on more complex systems as a whole. It has been pointed out that well defined procedures for the evaluation of papers are generally difficult to apply to more complex paper-polymer (e.g., fixative, adhesive, etc.) systems. But it is generally more important from the point of view of conservation to evaluate the system as a whole under conditions of (accelerated) aging.

Some of the foregoing test methods have been reviewed and discussed in a study on the examination of test methods for the evaluation of paper and paper conservation materials (5). In addition to describing the scope and limitation of some of the listed techniques, the absence of standards criteria and correlations among the testing procedures was noted. In that review, the importance of improving the diverse criteria for evaluation was emphasized as well as the importance of remaining open to new and improved techniques.

Technical Literature. In addition to the materials themselves the library would contain information as exhaustively and comprehensively as possible in the following areas:

1. Manufacturers' catalogs and technical data sheets together with additional manufacturers' test data provided on request by standard information format.
2. Formulations including recipes supplied by conservators.
3. Analyses independently obtained describing the contents of formulations.
4. Records of conservators' observations on the working properties of the materials.
5. A complete library of texts, monographs, and journals appropriate for the various materials science aspects and testing procedures of paper conservation.

The ready availability of this information to artists and conservators is of great importance. The possibility of extending this proposal for a repository-testing center to other areas of art conservation (e.g., textile; painting; stone; metal) is inherent in this idea. Access to this kind of information will prove invaluable to artists, conservators, and art historians.

GOALS

The goals of the testing and evaluative processes will be 1) to define the limits under which materials can be considered useful; 2) to describe hazards, faults, or difficulties associated with any materials; 3) to attempt practical ranking of groups of materials of similar composition or use; 4) to predict the effects of aging on the artifact; 5) to monitor quality of available materials; 6) to characterize materials with respect to composition and quantitative test results; 7) to provide comparative data for natural vs. accelerated aging; 8) to provide a sample collection for future generations of conservators and researchers; and 9) to study and establish ethical and practical standards for the use and application of materials and techniques of conservation.

CONCLUSIONS

Considerable valuable time has been lost due to the lack of adequately characterized samples of materials used in the past production and conservation of artistic and historic works. The continuously enlarged range of materials available makes it imperative that a major program be established to develop a repository for the materials of book and paper conservation. It is probable that only existing governmental agencies (e.g., National Bureau of Standards, Library of Congress) can adequately deal with this massive undertaking.

The authors are painfully aware of the inadequacy of this modest proposal and would much appreciate the comments of interested parties.

ACKNOWLEDGEMENT

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THE ESTABLISHMENT OF FINE ARTS RADIOGRAPHIC CENTERS:
RESULTS OF A PILOT STUDY

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ABSTRACT

A general program for the "Establishment of Fine Arts Radiographic Centers" has been described elsewhere. In this report, the authors present the results of a pilot study designed to compare the cost; ease of handling, storage, and production; and resolution for the range of formats available for the microreproduction of radiographs. These include 4"x5" or 100mm x 100mm film; Kodak Rapid Processing Copy Film SO-185; microfiche, microfilm, film jackets, and aperture cards.

For the pilot study, two sets of ten radiographs, one set from the Fogg Art Museum, Harvard University, the other set from the Conservation Center of the Institute of Fine Arts, New York University, were chosen for reproduction.

To present a wide range in contrast and format, each group included 14"x17" radiographs of: a painting on canvas requiring four films to radiograph the entire painting; a cradled panel with and without synthetic polymer beads filling the open space of the cradle; a series of watermarked papers; a polychrome sculpture; a ceramic object; and a small bronze.

After the initial production of the microform copies and a set of duplicates, the two sets of original radiographs were exchanged and the production of microforms was repeated in order to assess the savings associated with increased experience.

The results of this pilot study provide a valuable supplement to the data provided by microform suppliers.



TEXTILE CONSERVATION IN THE VICTORIA & ALBERT MUSEUM

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It is well known in the world of textile conservation that the department in the Victoria and Albert Museum has pioneered and developed the use of adhesives for the provision of support for fragile textiles further than any other museum in the world. The Central Research Laboratory of Amsterdam has been partner in this development, doing much needed research into suitable resins that have appeared on the market, testing their long term stability, and through the workroom in the charge of Mrs. Cassee providing a fruitful source of ideas for their use.

In this field, as in so many others, the exchange of ideas is very important. So often a slight modification of an already well used technique can provide the answer to a difficult problem, therefore in this report I intend to survey the background, growth and present usage of adhesives in the V. & A., acknowledging the source of the idea where appropriate. I shall also give a short account of the establishment and current working of a new tapestry section and the major project undertaken last summer of washing the Ardabil carpet.

The Textile Conservation Department in the V. & A. now has a full-time staff of 7 people, including myself. Two of these work on tapestries and carpets, one on costume and three on general items. There are also 2 full-time studentships occupied in the tapestry section, a part-time person for plain sewing work and another temporary part-timer for work on the Warner Pattern Books. My job is becoming increasingly administrative in character although I still do some active conservation whenever possible. At the time of writing there is a chance that staff will be expanded in the future.

These people handle between them upwards of 200 objects every year, varying in size, shape and complexity, most of which are required for a specific date for exhibition. In these circumstances time is as much a factor in the decision on method to be used as any other but is never allowed to be the over-riding factor if a slow method, i.e. sewing is obviously better for the object. When considerations are 50-50 the quicker method i.e. using adhesives, would probably be chosen.

It may seem that the argument 'sticking v. stitching' should long ago have been resolved but recent events in England have proved that this is not so and that facts well known to scientists should be repeated once more for the benefit of the non-scientific conservator and those new in the field.

In a recent report (from which I intend to quote extensively) I said, "Stitching methods are preferable when the main body of the textile is in sound condition, when it is heavy and of a complicated structure such as a triple weave brocade, or when a heat-sealed net would interfere too much with the drape of the material".

"Sticking methods are preferable when the main body of the textile is in a very fragile condition and when a stitching method would interfere too much with the visual appearance of the object. For instance, when a silk satin has reached a certain stage of deterioration it is in need of total support. This can only be given safely by attaching it throughout to a backing material by the heat-seal method. With a stitching method only the areas already broken up will be couched down to the support. Those that are still superficially intact will not be secured. Inevitably over the years the surface warps dust away, leaving the weft hanging loose. With this inevitable further degradation they split and further work will be needed. If attempts are made to stitch down the areas that are still intact as well as those manifestly decayed, not only will the visual effect be less satisfactory but also the fabric will be further weakened by the action of the needle and thread, however fine, in breaking through some of the fibres. It is easy to find examples of couching technique done in the past where areas once stitched down have vanished from beneath the stitches. Although it is virtually impossible to prevent the surface from dusting away, the splitting cannot take place if the warps and wefts at the back of the weave structure are closely held by an adhesive.

Interference with the drape of the material can in fact be minimised by careful choice of materials and methods of application.

In the instance of the satin quoted here it was also necessary to use couching threads to hold the surface wefts which could not be held by the adhesive on the back.

Further on in this report Mr. Brommelle, Keeper of Conservation, V. & A. has given a brief outline of the history of the use of the adhesive method with a survey of its scientific background.

"Natural textile fibres such as silk, wool, cotton and linen consists of long chain molecules which disintegrate under the action of light and pollutants, the textiles eventually becoming embrittled. In the 1950's attempts in Holland were made to preserve textiles in this decayed condition by impregnating them with colourless synthetic resins. The appearance was unsatisfactory because in a sense the textiles were more or less embedded in the resin. From 1957 onwards Mr. E.R. Beecher (1) in the V. & A. experimented with the heat seal method mentioned above where the perished material was not impregnated at all but merely attached overall to a fine net pre-treated with a thermoplastic adhesive resin. Only the fibres of the net were coated so that the textile was firmly pinned, as it were, to this net-work.

An adhesive resin for this purpose had to have a certain range of properties, including chemical stability particularly in regard to the effects of light and the atmosphere, a softening point at around 60° C. and a reasonable absence of tackiness at room temperature. Polyvinyl acetate introduced to the museum world in 1930 had these properties, but until the mid 1950's would have required the addition of a "plasticiser" to bring the softening temperature down to a safe level for use with textiles. The plasticisers had the disadvantage of migrating and evaporating from the resin, thus making it progressively more brittle and increasing the temperature needed for reversing the process should this ever be needed. Fortunately at around the time that the experiments were begun (1957) the method of so-called "internal plasticisation" was discovered. Dr. A.E. Werner writing at a later date in the Museums Journal, Vol. 64, 1964, after describing the disadvantage of plasticisers, summed up the position as follows "an important advance in this field was the introduction of synthetic resins which are said to be internally plasticised. This in fact is not a particularly suitable designation because actually these resins are co-polymers of a particular molecular structure which confers permanent inherent flexibility which will not change with age. For this reason internally plasticised resins are much to be preferred in conservation work because the flexibility is an inherent property of the resin and does not depend on additives".

In the earlier experiments in the V. & A. a co-polymer of vinyl acetate and vinyl caprate was used. This was later replaced, after

experimental work at the Amsterdam Laboratory had shown that it was better to employ a co-polymer of vinyl acetate and dibutyl maleate² and this is still in use.

It has been shown experimentally not to change in weight or flexibility either at room temperature or under prolonged heating. The textile can be lifted from the net after long periods either by application of heat or harmless solvents. Experiments additionally show that the resin is unaffected by light over long periods, and that the rate of fade of a range of dyed textiles is unchanged by backing with treated net. There is no known chemical mechanism for an alleged fading effect of dyestuffs by a resin of this kind. If there had been any effect it would of course have revealed itself by a net-work of fine lines of fading, readily discernible. The resin is also neutral on application, i.e. neither acid nor alkaline and remains so under test, so that neither the textile's fibres nor associated metal thread could be attacked from this source.

Most of the textiles in the museum are unhappily exhibited and stored in uncontrolled atmospheric conditions in the middle of London so that they provide a severe test."

It is on the basis of these assurances that the work of my department has been extended so far into this field.

METHODS AND MATERIALS

There have been no major new developments in recent years, at any rate that have come to my knowledge, and for a number of reasons connected with the immutable laws of nature it is difficult to imagine what any such developments might be. Finer, stronger, more stable materials perhaps, but the essential methods of sticking and stitching are likely to remain with us. The only alternative that presents itself is impregnation but up till now it has proved impossible to find a substance that can provide a film that is strong enough while remaining unnoticeable. Perhaps such a substance is on the brink of discovery, but on the present experience it seems unlikely.

Apart from a suitable resin already mentioned, the basis of the technique under discussion is a suitable supporting fabric. Materials made from synthetic fibres are the most suitable for treatment with a synthetic resin adhesive, as they are, in general, finer in weave and dimensionally more stable than those made from natural fibres. We have available to us two or three knitted nylon nets of different deniers and the two polyester fabrics made in Switzerland called stabiltex Nos. 0 and 4. (3). No. 4 is similar to silk crepe line except that it is whiter and slightly more opaque. No. 0 is locked weave fabric very suitable for upholstery and heavy materials. We also have a polyester woven net made in England which is thicker in denier and slightly more open in weave

and which we propose to use for tapestries. From the natural fibres we use silk crepeline for some purposes. Incidentally in the context of the use of natural or synthetic fibres we have gone over to using polyester sewing thread, made by GÜtermann-Perivale (4) in place of cotton and in some places of silk and linen as well. The wool, silk and linen for tapestry repairs, however, remain supreme.

The most important factor in the successful use of P.V.A. is the method of application to the chosen fabric. It should be known from my publications (5) that I favour the sponging method using a frame, for nylon net. It is possible using this technique to apply adhesive to both sides of the net so that it may be sandwiched between the object and a material used for extra support and to fill in missing areas with suitable colour and texture. In the case of furniture this extra backing provides something strong enough to take the strain of re-upholstery.

When simple storage is in question we use silk crepeline - the most transparent material available - to act as an isolator, to prevent treated net adhering to other surfaces during long periods of contact.

After a personal visit to Amsterdam where I was able to observe the technique closely, I have also become converted to their method of "painting out" on Melinex (6) when treating either silk or polyester crepeline with P.V.A. adhesive. My previous impressions had been formed by some very bad examples, which only goes to show how careful one must be when making judgements. Poor craftsmanship can easily put a perfectly respectable method into disrepute. This method gives a thin film of P.V.A. on one side of the crepeline which is more efficient for supporting very brittle materials. Some late 19th cent. weighted silk, taffetas and satins, glazed cottons and banner silks are frequently reduced to sharply defined fragments which tend to break away from nylon net.

Although I have already stated that impregnation with the purpose of embedding a textile in a film has so far proved unsatisfactory aesthetically there are two substances, polyvinyl alcohol and soluble nylon which have their uses.

APPLICATIONS AND REFINEMENTS

Soluble nylon gives little extra tensile strength to brittle fibres, tending rather to increase the brittleness but it is useful used as a spray on such surfaces as satin and velvet. Both satin warps and velvet pile can disappear in the form of dust which a 2% sol. of nylon in alcohol can help to prevent without being visible. It is possible to feel a slight stiffness in a velvet pile after treatment but this is a small price to pay for preservation.

75/10/1-6

In fact this treatment will help give cohesion to any fibre which has become rotten but has remained soft as opposed to becoming brittle.

Recently an embroidered satin bearing the last few traces of black embroidery thread had to be washed. The date was 17th cent. and thus there was the double risk of loosing the dusty fragments of thread and of the black dye being fugitive in water. A 4% sol. of soluble nylon was painted on the threads with a small paint brush before washing, with complete success. Another recent use was influenced by something seen in Amsterdam where they had the problem of cleaning some material bearing a design in paint. They had found that impregnating the painted areas with soluble nylon enabled them to wash the materials without loosing the paint. Faced with a similar problem of painted Chinese silk made up into cushion covers we tried the same solution also with success.

It is possible to fix down flaking oil paint on banner silk in this way as well, but it is necessary to follow up with heat and pressure applied on a vacuum hot-table. Polyvinyl alcohol is not widely used but can replace starch when muslins, lawns and lace have to be prepared for exhibition. To produce the full stiffening effect it is necessary to apply heat. Since it is very undesirable to iron lace we apply heat from a hand-held hair dryer.

A development in the use of P.V.A. based on an idea of H. Jedrzejska may prove of interest. In the chapter on archaeological textiles in Dr. Leene's book (7), Mme. Jedrzejska describes how she incorporates new warps and wefts by means of tiny spots of glue.

If, instead of using isolated spots of glue, fine silk or polyester threads are drawn through a pool of P.V.A. leaving thousands of tiny droplets of glue along the whole length, they can be used on the back of small fragmented objects as new warps and wefts, attaching them to the old ones by heat. This can be particularly useful when it is required to see the method of manufacture of the object on both sides.

Such threads can also be used on the surface of a fabric as a kind of couching, which is ironed into place instead of being stitched. This can be an occasional advantage.

Another idea for a different use of P.V.A. comes from Amsterdam and this is to make a separate film, casting it on a sheet of Teflon-coated glass cloth from which it will peel easily. This is not so easy as it sounds! The P.V.A. does not wet the non-stick surface of the Teflon but tends to ball up. The surface must be warmed and the liquid brushed out quickly. The film thus created can be used to fuse an old fabric and a new support together without the need for a third intermediate material.

The occasions when this is necessary are firstly if it is required to roll the resulting sandwich or, as in the case when I used it myself, when large areas of object are missing and the supporting net has to be cut away for appearance sake. This can leave an ugly hard outline where it is cut. The film, on the other hand, can be pulled away from a hot iron leaving a clear contour.

A NEW SECTION

During the past three years we have been able to expand and develop the work of the tapestry section with the completion of a new building and the installation of new machinery for washing and supporting heavy objects. Two extra staff were employed expressly for work on tapestries and carpets and these have been further augmented by 2 students who will work in the department for 4 years.

The section is now in full operation using a variety of techniques for repair including the adhesive method. This method is so far restricted to tapestries of secondary importance which would take more time than they are worth to repair by conventional methods. The machinery installed for washing was first described at the Delft Conference in 1964 but was not in operation until 1972. A number of difficulties had to be overcome but it is functioning efficiently now. However, the largest object the machine can carry is approx. 4.3m x 6.5m so that when faced with the Ardabil carpet, which is approx. 5.5m x 11m, we had no choice but to take it elsewhere to wash.

THE ARDABIL CARPET

There is nowhere within the Museum premises to wash such a very large object so we had two alternatives - either to use the grounds on an out-station belonging to the Museum, in the London area, which could have meant providing pure water as London water is so hard and chlorinated, or to travel further afield and take the carpet to an area where soft water is on tap.

The first alternative was technically difficult as it entailed fixing a water purification unit to a fire-hydrant outside Osterly Park House while the second was very tempting as The Keeper of Conservation at Birmingham, Mr. Stephen Rees-Jones, was willing and able to help us. The water in the Birmingham area is very good and a site was found for us in the courtyard of a 16th cent. manor house in the outskirts of the town. Since I hope that this episode will be illustrated by film at the Conference I shall only give a brief outline of our procedure here.

A local firm built a sloping platform from scaffolding in the courtyard where water could drain away freely.

75/10/1-8

This platform was covered with polythene sheeting before the carpet was placed face downwards upon it. Water was applied from a hose with a garden spray attachment and detergent solution worked into the surface with industrial lambs-wool paint rollers on broomhandles. Since it was inevitable that we should have to walk on the carpet it was first covered with a coarse net and each worker wore rubber boots with sponges stuck to soles and heels. The carpet was washed 3 times on the back, drained overnight, turned over and washed 3 times on the front on the following day.

The detergent used was a pure anionic one, provided by Unilever, formed from a mixture of ammonium lauryl ether sulphate and sodium alkyl benzene sulphonate.

Mrs. Judith Hofenk de Graaff, who has done so much work in this field (8), was consulted on our choice, and assured us that there was no reason to suppose that any minute traces remaining would cause any long term damage.

This choice of an anionic rather than the more usual non-ionic detergent was governed by several factors. It is a well established fact that an anionic detergent is the more efficient cleaner and since the carpet was very dirty and our time limited it seemed sensible to choose that which would work fastest. Previous experiments showed that the general feel and look of the wool pile was better than with any other we tried and finally the fugitive colours of old repairs, which were impossible to remove completely, seemed less likely to run.

We used Mrs. Hofenk's standard recipe (8) containing S.C.M.C. and a tri-polyphosphate although we increased the amount of the latter by 0.5g/l to take account of any unknown salts that might be present in the water.

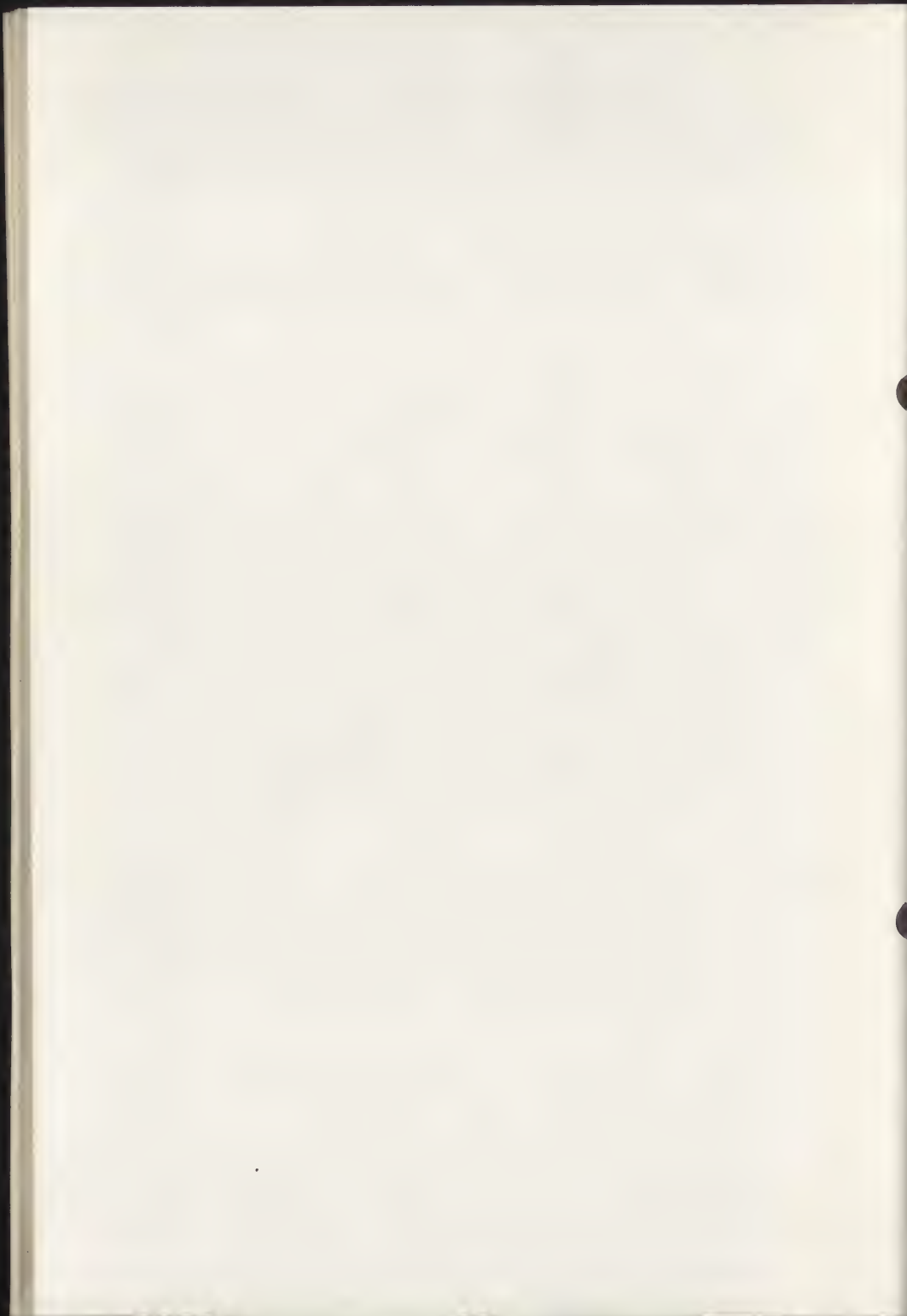
The final result was very satisfactory.

The repairs to the carpet will take a long time to complete but by the time of the Conference I hope to be able to report fully on what has been done.

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ARTIFICIAL AGEING OF YARNS IN PRESENCE AS WELL AS IN
ABSENCE OF LIGHT AND UNDER DIFFERENT ATMOSPHERIC
CONDITIONS - Condensed final report

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A B S T R A C T

Several natural textile materials have been subjected to artificial ageing processes. The influence of light, temperature, humidity, air pollutants, several pre-treatments, and combinations of these factors have been investigated. The results are discussed in general, and conclusions and recommendations are given for storage and exhibition of textile museum objects.

I N T R O D U C T I O N

At previous occasions we already delivered interim reports on a research project dealing with artificial ageing of textile materials (1), (2), (3), (4). The project was carried out at the Laboratory for Textile Technology of the Delft University of Technology, Holland, in cooperation with the Central Research Laboratory for Objects of Art and Science, Amsterdam, Holland.

As was stated at the meeting of the working group Textiles of the ICOM Committee for Conservation at Madrid, October 1972, the research project had to be terminated by 1974, because then a reorganisation would take place at the Laboratory for Textile Technology. This had as a result that during the last two years no further information from new experiments could be obtained. Our main effort has been the arrangement of the thousands of analytical data (especially those of wool) collected during the foregoing years, in such a way that it would enable us to draw general conclusions. Most of the preliminary results, as reported in the 4th Interim Report (4), are still of value.

Since presentation of the results in the form of tables and graphs would cover hundreds of pages, we will restrict ourselves to a condensed review of materials tested, ageing procedures and analytical

75/10/2-2

methods used, and to the ultimate conclusions. A detailed working programme has been published in (2) and (3).

It may be noted here that from the start the project was set up to give museum conservators and curators scientifically based recommendations for the best way of exhibition and storage of the textile objects in their possession; in general terms this aim has more or less been attained.

On the other hand, however, the vast amount of analytical data gathered may also be of value in theoretical chemistry. Actually, a theoretical model for the degradation of cotton cellulose was developed from our data. It would be beyond the scope of this report to discuss this model here. This has been done elsewhere by Elema c.s. (5), (8).

Now it is unfortunately beyond our capacity - by lack of manpower - to treat all information we gathered during the last ten years in such a way as to arrive at hypotheses or theories concerning the degradation mechanisms of the investigated textile materials from a chemical point of view. Therefore we gladly invite any scientist to do so on the basis of our data and our internal reports. We will give him or her full access to these data and reports in every detail and we shall give any possible support. Interested parties are cordially invited to contact the Central Research Laboratory for Objects of Art and Science, Gabriël Metsustraat 8, Amsterdam, Holland, through which all information is available.

AGEING METHODS (See Table 1)

The conditions under which the materials were aged artificially were chosen in such a way that the ageing process was accelerated while at the same time it could be expected that no degradation reactions would occur different from those taking place in a natural ageing process. Ageing of the various textile materials was performed in three different apparatuses (see also all four Interim Reports).

1. conditioning stoves, in which - in the dark - temperature and relative humidity of ambient air could be variegated.
2. irradiation apparatuses, in which fluorescent tubes with different spectral energy distributions could be placed; the atmosphere surrounding the materials to be tested could be variegated: ambient air, purified ambient air, purified air with known amounts of air pollutants added.
3. virtually the same apparatuses as under 2, but without a light source.

75/10/2-3

apparatus	light source	temperature °C	relative humidity %	atmosphere				
				ambient air	purified air			
					without addition	ca. 5 ppm NO ₂ added	ca. 20 ppm SO ₂ added	ca. 0.3 ppm O ₃ added
1. conditioning stove	-	55	10	+				
	-	55	90	+				
2. apparatus with fluorescent tubes	TL 34	39	22	+				
	TL 37	39	22	+				
	TL 57	39	22	+				
	TL 8	39	22	+				
	TL 57	45	21		+			
	TL 57	45	21		+	+		
	TL 57	45	21		+		+	
	TL 57	45	21		+	+	+	
	TL 57	45	21		+			+
	TL 57	45	<0.05		+			
	TL 57	45	21		oxygen-free nitrogen ca. 1 ppm O ₂			
3. apparatus without fluorescent tubes	-	45	21		+			
	-	45	21		+	+		
	-	45	21		+		+	
	-	45	21		+	+	+	
	-	45	21		+			+

TABLE I Ageing methods

75/10/2-4

M A T E R I A L S

All textile materials were in the form of yarns.

Cellulose yarns: raw cotton, bleached cotton, scoured mineral khaki dyed cotton, quarter-bleached linen.

Protein yarns : wool rinsed with water, wool extracted with diethyl ether or dichloromethane (methylene chloride), wool washed with several soaps or detergents, wool after washing treated with formic, acetic and sulphuric acid respectively, at different pH-values (acidity), wool dyed with several chrome mordanted natural dyes and a natural vat dye, silk.

A N A L Y T I C A L M E T H O D S (for more details see (3) and (4))

After a certain period of degradation (for cellulose yarns mostly after 8 weeks, sometimes up to 24, and occasionally up to 215 weeks, and for wool mostly after 1 to 24 months, sometimes 60 months) samples were taken from the yarns and these samples were studied. From all yarns the tenacity (specific strength, in gf/tex), either at 50 cm or at zero cm testlength or both (the latter being a good measure of fibre material strength), and the breaking extension (in %) were determined. In addition, for cellulose yarns the degree of polymerization was determined from which the average number of molecule scissions can be calculated, and for wool we determined the changes in the amount of sulphur containing amino acids present (cystine, cysteine and cysteic acid¹). For some highly aged materials the fibre density, the moisture sorption and the swelling properties were determined. For the greater part the conclusions are based on changes in the above-mentioned properties.

D I S C U S S I O N O F R E S U L T S

VALIDITY

As stated before (3), (4), strictly speaking our conclusions are valid only for the materials and methods investigated. All along the line, however, we feel rather sure that the following general conclusions have a greater validity and this for two, rather contradicting reasons. On the one hand we found that the behaviour of a textile material during ageing greatly depends on its previous history, such as (unknown) pre-treatments, dyeing, or foregoing me-

1) Changes in content of many other amino acids were also determined but not taken into consideration, since the information gathered therefrom did not help much in the interpretation of the results as seen from a conservator's point of view.

chanical tensions. This means that an exact prediction of the behaviour during ageing of a specific material can not be made. On the other hand in general the ageing methods applied had comparable effects on materials, in a chemical sense so different from one another as are cotton and wool.

INFLUENCE OF AGEING FACTORS

Influence of light

a. Spectral energy distribution: This distribution is of marked influence. The more ultra-violet (UV) the light source emits, the more damage is caused. We used Philips fluorescent tubes as a light source, which, when arranged in increasing amount of UV radiation emitted, had colour codes TL 37, TL 34, TL 57 and TL 8 (nearly pure UV) respectively. Put in the same order these tubes caused relative severity of degradation (based on number of molecule scissions) on bleached cotton of roughly 1 : 2 : 3 : 5 respectively.

But with tubes without UV emission degradation also occurs, and even the infra-red emission is not harmless as was shown by Daruwalla (6). We carried out most of our experiments with TL 57 tubes. b. Intensity: The degradation power of light is expected to be proportional to the incident light intensity, which was confirmed by some special tests. In our experiments the intensity was mostly about 3000 lux, that is ca. 80 cal/cm²/day.

We found that light is the most harmful of all degrading factors investigated. This means that in museums the light intensities have to be kept at a level as low as possible, of course without decreasing the perceptability too much. In fact these findings strongly support the 150/50 lux maximum illumination level recommended by the Working Party on Lighting of the ICOM Committee for Conservation (7). Where textile materials are concerned, which are so vulnerable, the 50 lux level should not be exceeded.

c. Effect of dyeing the materials: On the basis of our experiments with dyed yarns we can state that in several cases dyes will protect the textile materials to some extent against degradation under the influence of light. This can be explained by the light absorbing capacity of these dyes. On the other hand the dyes showed much fading. These results are interesting to know, but in fact they are of no practical value in the conservation of museum objects.

Influence of temperature

At increase of temperature the rate of degradation increases as well, not, however, as much as may be expected. A rise in temperature from 43° to 57°C in an irradiation experiment (TL 57) caused 30% more degradation in cotton (based on the number of molecule scissions). On this basis we have good grounds to say, that it seems not necessary to decrease the temperature in store rooms, etc. by costly technical devices, and that a storage temperature of about normal room temperature (e.g. 18 - 20° C) is acceptable. Keeping the temperature at

75/10/2-6

a much lower level than 20°C (e.g. 10 - 15°C) may diminish the danger of interference by insects. One should always be aware of the rise in temperature that may be effectuated in the textile materials themselves, especially when these have dark colours, by incident light from spotlights, sunshine, etc.

Influence of relative humidity

We found that high relative humidity (R.H.) of the atmosphere (about 90% R.H.) cause more damage than a low R.H. (about 10% R.H.). On the other hand a very low R.H. (less than 0.05% R.H.) also causes more damage than a somewhat higher R.H. This means that extremely low and high R.H. should be avoided. One should keep in mind that a relatively small increase in temperature, such as caused by heat generated by a light source, will result in a rather high drop in R.H. in the microclimate of the object. A relative humidity of the atmosphere of 50 to 60% (55 ± 5% R.H.) is generally accepted as suitable. Higher humidities may lead to mildew growth, etc. For reasons explained under "Swelling" of this report rapid changes in relative humidity should be avoided.

Influence of air pollutants

Air pollutants will always cause more or less extra damage, in the dark as well as under irradiation. The seriousness of this extra damage is, however, hardly predictable; in some cases the effect was rather small, in other cases heavy damage occurred. For sulphur dioxide and nitrous oxides we used pollutant concentrations of about 50 times the highest ever measured values in an industrial area (Rotterdam, 1965), for ozone about just as high as the highest measured value. We also investigated the combined effect of sulphur dioxide and nitrous oxides, which in some cases caused more, and in other cases less damage than each of the pollutants separately. The conclusion can be that removal of air pollutants from the air is advisable, but in our opinion it is in many cases not a direct necessity, except when the museum is situated in a highly polluted area. When a central airconditioning system with airwashers is installed, air pollutants are generally removed to an acceptable level.

Influence of oxygen

When the degradation reactions are oxidative in character, it is to be expected that decreasing the oxygen content in the surrounding atmosphere will decrease the rate of degradation. This indeed is true, but in the case of cotton under irradiation we found that the relation between the rate of degradation (based on the number of molecule scissions) and the oxygen concentration is not linear, but seems to be logarithmic in character. This means that if we want to effectuate a considerable decrease in oxidative degradation, we will perhaps have to reduce the oxygen concentration to the level of parts per million. It is technically a very difficult and costly

job to maintain such a virtually oxygen-free atmosphere over long periods, and therefore this is unrealistic in normal museum practice. Only for very precious objects it could be worth considering.

Influence of mechanical tensions

Although we did not in fact investigate the phenomenon, we have strong indications, also on theoretical grounds (5), that mechanical tensions will increase the rate of degradation. An important degradation mechanism is the breaking of chain molecules in the material. The occurrence of these breakages will, by an activation mechanism, increase when the chain molecules are under tension, generated by internal or external causes. This may explain that we often find a more advanced deterioration in folds and creases, in the upper part of tapestries, etc., the effect being enhanced by other factors. It is therefore advisable to subject textile materials as little as possible to mechanical tensions such as bending, folding and hanging by its own weight without support. The best way to avoid folding (also for other reasons, e.g. permanent deformation) is to roll the cloth on a cylinder of acid-free cardboard with a minimum diameter of 100 to 150 mm. See also under "Tenacity and breaking extension" and "Swelling" of this report.

Combined influence of ageing factors

We found that in several cases the effect of one ageing factor can be intensified by another. So for cotton, irradiation in the presence of air pollutants caused a damage larger than the addition of the damages (measured separately) originating from light in purified air, and from air pollutants in the dark.

Special remarks on cotton and linen

The main result of the degradation of these cellulose materials is the "breaking" of the macromolecular cellulose chains, with resultant loss of strength. The formation of extra functional groups could not be detected by our analytical methods (e.g. infra-red spectroscopy). This is understood because one molecule break causes chemical change only in two out of about 7000 monomer units in the chain molecule.

Special remarks on wool

- a. In the 4th Interim Report (4) we announced a thorough treatment of the assessment of the degradation in terms of a so-called overall "rate of degradation". While we were treating our analytical data, however, we got more and more convinced that it would be too high-pitched to look for a specific rate of degradation for every ageing method and every treatment. We found it of more value to look for similarities than for differences in behaviour. This does not mean that our conclusions in the 4th Interim Report (see par. 3.3.2. and 3.3.3. in (4)) are no longer valid, but we now have worded them slightly differently.

75/10/2-8

- b. Left-over remains of natural soaps and anionic and nonionic detergents (after washing and rinsing) did not cause much extra damage. The degradation occurred in much the same way as in wool rinsed with water only. This means that washing with these soaps and detergents in itself is allowed, see, however, under "Solubility" of this report.
The use of domestic detergents must be strongly discouraged, since they will mostly contain bleaching agents (and optical brighteners) which are unsuitable for ancient textiles because they cause heavy damage.
- c. If for some reason (for instance in a dyeing process) wool has to be treated with an acid, it is to be preferred to use an organic acid such as formic or acetic acid. With these acids the acidity (pH) of the wool has little or no influence on the degradation in the dark, and besides the rate of degradation is not accelerated; it may even be slightly decelerated. Treatment with sulphuric acid is to be discouraged, because under certain circumstances degradation may be increased.
- d. Extraction of wool with a solvent (as will happen in a dry-cleaning process) will increase degradation. In our experiments we used diethyl ether and dichloromethane, which caused rather heavy damage in the dark, especially at higher relative humidities.

Special remarks on silk

We made only very few experiments on silk. From these it was clear that silk is very prone to degradation under the influence of light. In a period of 8 weeks under irradiation a loss in tenacity of ca. 60% occurred.

EFFECTS OF AGEING ON SOME PHYSICAL PROPERTIES

Tenacity and breaking extension

The most distinct and directly observable changes in properties effected by ageing are a loss of tenacity and a heavy loss of breaking extension (elasticity) of the yarn (and likewise of fibres and fabrics). Because both tenacity and breaking extension decrease, the capacity of the yarn to absorb mechanical energy (work of rupture; toughness) under tension decreases sharply. The yarns tend to become brittle, fibres drop off the yarn, sharp bends and folding cause breakage. After advanced ageing it became nearly impossible for our laboratory workers to handle the yarns without breaking them. In our opinion it is not so much the loss of tenacity that causes the difficulties in handling ancient fabrics, but more the loss of energy absorbing capacity. Again this means (see also under "Influence of mechanical tensions" of this report) that, especially with ancient textiles, sharp bending and folding should be avoided.

Coefficient of friction

Another property that may change by ageing is the coefficient of friction, which increases. The material gets harsh to the touch. This increase of the coefficient of friction may induce an increase in tenacity of the yarn at a testlength of 50 cm, but in fact the material strength (measured at zero cm testlength) has decreased.

Solubility

As reported earlier (4) an unexpected result of our investigations was that textile materials appeared to become partly dissolvable in water after advanced ageing. From a wool sample irradiated during 48 weeks with TL 57 in a very dry atmosphere (heavy damage) 16.5% by weight dissolved in water, a linen sample irradiated during 215 weeks in ambient air dissolved for 13.1%, and a cotton sample irradiated 132 weeks dissolved for 9.6%. Ancient textiles degraded by natural ageing are also partly dissolvable in water. We investigated cotton and linen from 50 to over 3000 years old, and each sample contained some water-extractable material, from 2% to about 15% by weight. In the case of cotton the extractable matter showed the presence of glucose which is evidently a degradation product of cellulose.

Most of the soluble degradation products will dissolve during the first few minutes after immersion in water. Not out of place here is a warning to the effect that highly deteriorated textiles will suffer considerable loss in weight during washing. Washing and rinsing should therefore be avoided, unless there are very good reasons for doing otherwise.

Hygroscopicity, density

The hygroscopicity (the measure of absorption of moisture from the atmosphere; regain) of wool, linen and cotton is also changed by ageing. The water sorption curve changes its form: at medium humidities (about 65% R.H.) less water is absorbed, at high humidities (about 99% R.H.) more water is absorbed than in unaged material. After extraction of water soluble material, however, in the medium part of the curve the regain is higher, and at high humidities the regain is lower than for unextracted aged material. These phenomena may be explained by the hygroscopicity of the extractable products, and by the fact that we found that the density of the fibre materials (as measured by means of the helium gas method) increases by ageing. The latter, as well as the changes in the water sorption curves, means that structural changes take place in the fibres during the ageing process. The character of these changes are as yet unknown. Wool seems to be more subject to structural changes than cotton.

Swelling

It is well known that natural fibres swell when they take up water from the atmosphere and when they are wetted. If the fibres are in

75/10/2-10

a twisted yarn structure (and the yarn in a fabric) this swelling causes the yarn to contract (with hemp we found a contraction of 5 - 6%). When the yarn is kept at a fixed length (e.g. in a fabric fixed with pins) the contraction force causes stress in the yarn and consequently in the fibre material (in the hemp yarn this stress was about 1 kg per mm² material cross-section). It might be feared that these tensions will cause fibre breakage in highly degraded textiles and thus will be harmful.

We made some special experiments with highly tendered cotton fabric (artificially degraded by acid hydrolysis, loss of tenacity ca. 85%, loss of breaking extension ca. 53%). We subjected this fabric to 25 cycles of immersion in water with subsequent tensionless drying. After this rather rough treatment the fabric did not show any significant symptoms of extra tendering. We may thus expect that the swelling forces, whether originating from moisture uptake from the air or from immersion in water, are not great enough to cause fibre breakage, provided the fabric (or yarn) is allowed to contract freely.

The remarks made under "Influence of mechanical tensions" of this report, however, keep their validity. For this reason we feel that rapid changes in relative humidity of the atmosphere should be kept at a minimum. This is because rapid changes in relative humidity will evoke rapid changes in swelling forces, which in their turn may effectuate mechanical tensions in (a part of) the chain molecules of the textile material. As we have seen under "Influence of mechanical tensions" these tensions may cause extra damage by molecule break. When slow changes in relative humidity take place (e.g. seasonal changes within the boundaries of 45 to 60% R.H.) the relaxation phenomenon will decrease the tensions caused by swelling, and by this mechanism slow changes in relative humidity seem to be less harmful.

CONCLUSIONS AND RECOMMENDATIONS

Partly quoting from (4) we may conclude as follows:

1. The rate of degradation of a textile material, wholly or partly consisting of cotton, linen and/or wool, is hardly predictable, even when the ageing factors of the environment are known.
2. To retard degradation certain precautions may be taken:
 - a. Exclusion of light as far as possible, also of infra-red and especially of ultra-violet radiation, because the degrading effect of irradiation is much larger than the effects of any of the other degrading factors. The exclusion of light is the most important weapon against the degradation of textile materials.
 - b. Avoidance of higher temperatures, originating from light incidence, central heating, sunshine, etc.
 - c. Avoidance of extremely low and of high relative humidities, and of rapid changes in relative humidity.

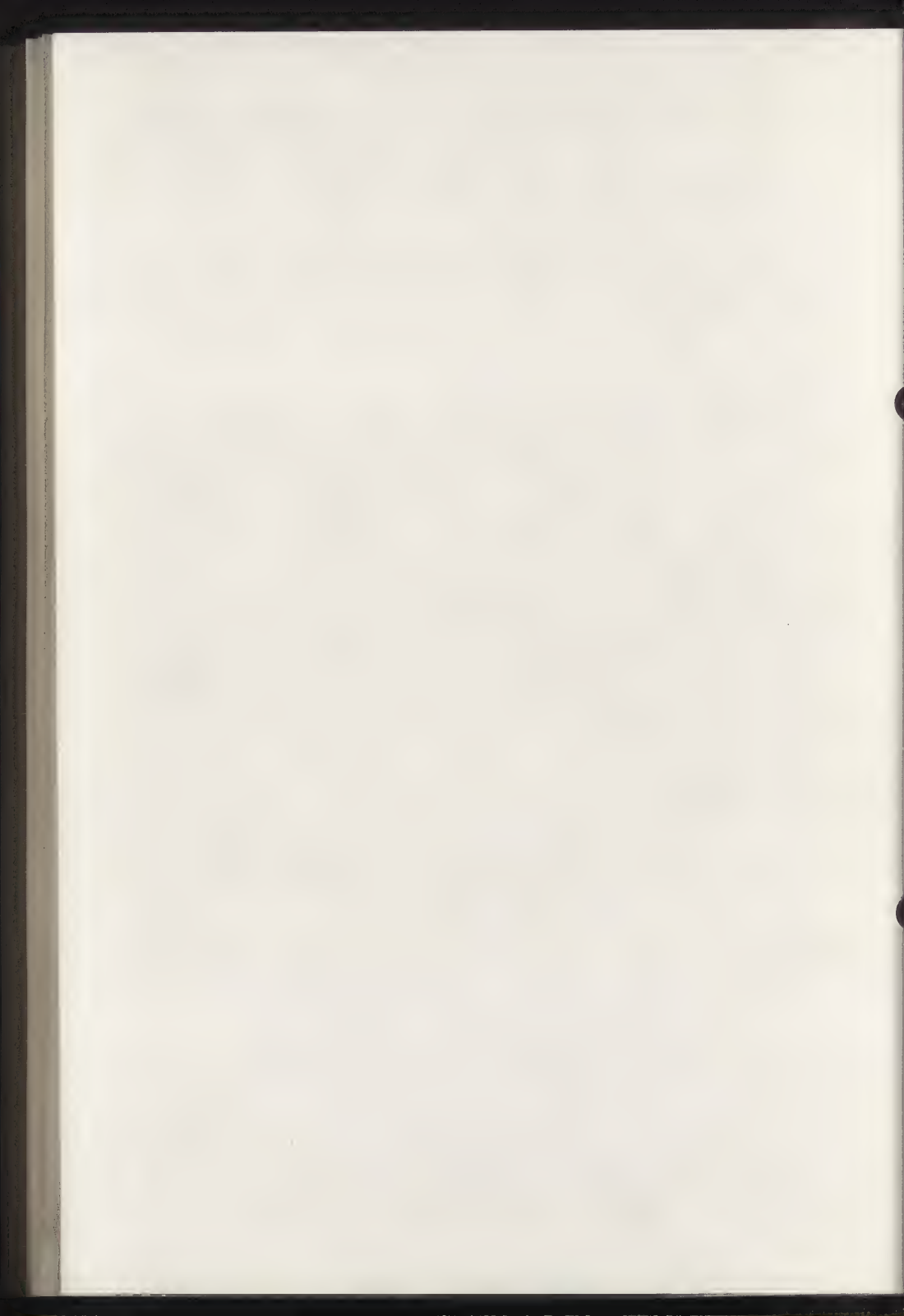
- d. Removal of air pollutants from the atmosphere.
- e. Avoidance of material stresses.
- f. Reduction of the oxygen concentration in the surrounding atmosphere to the level of a few hundred parts per million, or preferably less. This will only be feasible for very precious objects.
3. Highly degraded textiles proved to be partly dissolvable in water. Consequently one has to be very cautious in washing ancient textiles.
4. The ageing process causes structural changes in natural textile materials, resulting in somewhat increased density, and in a change in character of the water sorption curve.
5. When an investigation is made in the influence of any degrading factor as such (e.g. air pollutants, temperature, humidity or chemical agents), the experiments should be made in the dark. This is because the degrading power of light is so large, that it is apt to overshadow the effects of the degrading factor under investigation, and because light may have an intensifying influence as well.

A C K N O W L E D G E M E N T

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**'WOVEN BOUQUET': DYESTUFF-ANALYSIS ON A GROUP OF NORTHERN
DUTCH FLOWERED TABLE-CLOTHS AND TAPESTRIES OF THE 17th
CENTURY**

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INTRODUCTION

Dutch 17th-century table-cloths are quite rare. Of the total production, which in that prosperous era is known to have been abundant, about 50 specimens are left. They are now dispersed over several museums and private collections. In 1969 and 1972 exhibitions ("Woven Bouquet") of these table-cloths and tapestries were held in the Danske Kunstindustrimuseet in Copenhagen and in the Rijksmuseum in Amsterdam respectively (1,2). Almost all table-cloths and tapestries still preserved were displayed at those exhibitions. It is generally assumed that most of these objects originate from the towns of Gouda and Delft.

The Dutch contribution to tapestry-weaving began around the middle of the 16th century. After the fall of Antwerp (1585) many weavers from Flanders (3) settled in the Netherlands, especially in Middelburg, Delft, Gouda and Schoonhoven. A weaver of particular renown at the time was Frans Spiering in Delft. Many of the Dutch flowered tapestries were made on commission and a substantial amount was exported to Scandinavia, so it is not surprising that about one third of the preserved tapestries and table-cloths remained there. Considering their appearance the tapestries and table-cloths can be divided into groups (1). Some of them have the date woven in the hem. Those without (the major part) cannot be dated with precision and their manufacture is presumed to have taken place between 1630 and 1670.

AIM OF THIS RESEARCH

After having finished research on red dyestuffs (period 1450-1600) it turned out that a lot of data with regard to origin and date were missing, which became clear in the course of the statistical process of analytical results. As a consequence it was impossible to give more than a rough estimation of the analysed results ob-

75/10/3-2

tained. Thanks to the kind cooperation of private owners and museum curators it was made possible to take samples of almost all table-cloths and tapestries since they were exhibited at the Rijksmuseum in Amsterdam in 1972 and to subject them to analysis of their dyestuffs. The aim of this research is to find out whether there is a group of table-cloths which might be traced back to one single workshop and to determine whether some specimens may have been woven after the presumed period of manufacture, 1630-1670, with the use of established cartoons.

METHODS OF RESEARCH

For the analysis of dyestuffs and mixtures thereof thin-layer chromatography was selected. In previous research projects this method proved to be one of the best where used on textile materials (4,5). Samples are to be kept very small, so that no damage can be done to the object.

ANALYTICAL PROCEDURE (4,5)

The sample is boiled with a drop of 10% hydrochloric acid, in order to decompose the metal-dyestuff complex (mostly red and yellow dyestuffs are mordant dyestuffs). After hydrolysis a drop of methylalcohol is added to dissolve the dyestuff. This solution is used for the analysis. The conditions under which the analyses are carried out are as follows:

- Red dyestuffs : Pre-coated sheets of Messrs. Macherey & Nagel: type Cel 300 AC 10;
Eluent: tetrahydrofuran/ethylacetate/water/ 35:6:45.
Detection: Spraying with 0.5 normal solution of KOH in methylalcohol, and observation under U.V. light, 350 nm.
- Yellow dyestuffs : Precoated sheets of Messrs. Macherey & Nagel: type: MN-Polygram Sil G.
Eluent: toluol/ethyl formate/formic acid/5:4:1.
Detection: Spraying with 1% alcoholic solution of Naturstoff-Reagens A(Fluka, 2-aminoethyl-diphenylborate) and observation under U.V. light, 350 nm.
- Blue dyestuffs : Indigo and Woad are not analysed by means of thin-layer chromatography, but reduced to their Leuco-form and identified by shaking with ethylacetate (6).

SAMPLING

Of all table-cloths, tapestries and upholstery made available for the purpose, we took samples of all shades of colours and as much as possible from the reverse of the objects. Of the upholstery of chairs

samples were removed from arm-rests as well as from seats. From many tapestries often also the fringes were sampled. These were often of a later date. From one single tapestry we often took samples of more than one shade, such as three or four shades of red, because different mixtures of dyes have been in use. The total amount of samples was about 1500.

DESCRIPTION OF THE TAPESTRIES (1).

1. Table-cloth, wool and silk, warp-thread of linen; 183 x 310 cm., second part of the 17th century, Cat. nr. 1.
Owner: Rijksmuseum, Amsterdam (16495 A).
2. Table-cloth, wool and silk, 210 x 255 cm, North-Netherlands, middle of the 17th century, Cat. nr. 2.
Owner: The King and Queen of Denmark.
3. Table-cloth, wool and silk, warp-thread of linen; 170 x 270 cm., North-Netherlands, middle of the 17th century, Cat. nr. 3.
Owner: Stedelijk Museum "Het Prinsenhof", Delft.
4. Table-cloth, wool and silk, warp-thread of linen; 160 x 217 cm., North-Netherlands, middle of the 17th century, Cat. nr. 4.
Owner: Victoria and Albert Museum, London.
This table-cloth was probably woven after the same cartoon as under number 3.
5. Table-cloth, wool and silk, warp-thread of linen; 214 x 271 cm., North Netherlands, second part of the 17th century, Cat. nr. 5.
Owner: Stedelijk Museum "Het Prinsenhof", Delft.
6. Table-cloth, wool and silk, warp-thread of linen; 160 x 264 cm., North-Netherlands, first part of the 17th century, Cat. nr. 6.
Owner: Mayorcas Ltd. London.
7. Table-cloth, wool and silk, warp-thread of linen; 240 x 343 cm., North Netherlands, 1650 - 1670, Cat. nr. 7.
Owner: Koninklijke Musea voor Kunst en Geschiedenis, Brussels (inv. nr. 120).
8. Table-cloth, wool and silk, warp-thread of linen; 162 x 276 cm., North-Netherlands, middle of the 17th century, Cat. nr. 9.
Owner: Det Danske Kunstindustrimuseum, Copenhagen (1/1964).
9. Table-cloth, wool and silk, warp-thread of linen; 196 x 325 cm., North-Netherlands, first part of the 17th century, Cat. nr. 10.
Owner: The Duke of Schleswig-Holstein, Glücksburg.
10. Table-cloth, wool and silk, warp-thread of linen; 173 x 274 cm., North-Netherlands, first part of the 17th century, Cat. nr. 11.
Owner: Foundation Huis Doorn, Doorn, Holland.

75/10/3-4

11. Table-cloth, wool and silk and some metal threads, warp-thread of linen; 200 x 280 cm., The table-cloth is signed with an unidentified monogram TCDE and the date 1652.

Owner: Rijksmuseum, Amsterdam.

12. Table-cloth, wool and silk, warp-thread of linen; 240 x 343 cm., North-Netherlands, 1650 - 1670, Cat. nr. 13.

Owner: Det Danske Kunstindustrimuseet, Copenhagen.

13. Table-cloth, wool and silk, warp-thread of linen; 170 x 265 cm., North-Netherlands, third quarter of the 17th century. Probably by Spiering, Delft, Cat. nr. 14.

Owner: Holmenskirke, Copenhagen.

14. Table-cloth, wool and silk, warp-thread of linen; 212 x 278 cm., North-Netherlands, third quarter of the 17th century, Cat. nr. 15, Owner: J.M.M. Thompson Esq. Bridgnorth (Shropshire) England.

15. Table-cloth, wool and silk, warp-thread of linen; 174 x 340 cm., North-Netherlands, 1650 - 1670, Cat. nr. 16.

Owner: Statens Historiska Museet, Stockholm (inv. nr. 5302:18).

16. Table-cloth, wool and silk, warp-thread of linen; 203 x 225 cm., North-Netherlands 1650 - 1670, Cat. nr. 17.

Owner: Röhsska Konstslödmuseet, Gothenburg.

17. Table-cloth, wool and silk, warp-thread of linen; 206 x 264 cm., North-Netherlands, third quarter of the 17th century, Cat. nr. 18.

Owner: Vestlandske Kunstindustrimuseet, Bergen (Norway).

18. Table-cloth, wool and silk, warp-thread of linen; 227 x 331 cm., North-Netherlands, middle of the 17th century, Cat. nr. 19.

Owner: Rijksmuseum "Muiderslot", Muiden (Holland). (inv. nr. M.1957-1)

19. Table-cloth, wool and silk, warp-thread of linen; 194 x 215 cm., North-Netherlands, middle of the 17th century, Cat. nr. 21.

Owner: Rijksmuseum, Amsterdam (A 40, on loan from the Koninklijk Oudheidkundig Genootschap).

20. Table-cloth, wool and silk, warp-thread of linen; 194 x 275 cm., North-Netherlands, middle of the 17th century. The pattern of this table-cloth is about the same as that of nr. 19. Cat. nr. 22.

Owner: Rijksmuseum, Amsterdam (A 41, on loan from the Koninklijk Oudheidkundig Genootschap).

21. Table-cloth, wool and silk, warp-thread of linen; 172 x 235 cm., Gouda, Abraham Adriaensz. Goossens (?), 1670. Cat. nr. 23.

Owner: Stedelijk Museum "Het Catharina Gasthuis", Gouda.

22. Table-cloth, wool and silk, warp-thread of linen; 202 x 245 cm., North-Netherlands, middle of the 17th century. This table-cloth is probably the same as mentioned in the inventory of the "Deutzenhofje", dated 15th september 1700. Cat. nr. 24.

Owner: Regenten van het "Deutzenhofje", Amsterdam.

23. A strip of tapestry, wool and silk, warp-thread of linen; 68 x 217 cm., North-Netherlands, middle of the 17th century, Cat. nr. 25.

Owner: Stedelijk Museum "Het Prinsenhof", Delft (1960, XII, 26).

24. Table-cloth, wool and silk, warp-thread of linen; 221 x 270 cm. North-Netherlands, middle of the 17th century, Cat. nr. 26.

Owner: H.M. Queen Juliana, Paleis "Het Loo", Apeldoorn.

25. Table-cloth, wool and silk, warp-thread of linen; 264 x 312 cm. North-Netherlands, third quarter of the 17th century. Cat. nr. 27.

Owner: Gemeentemuseum, 's-Gravenhage (inv. nr. OW 2-65).

26. Table-cloth, wool and silk, warp-thread of linen; 176 x 242 cm. North-Netherlands, third quarter of the 17th century. Cat. nr. 28.

Owner: Residenzmuseum, Munich.

27. Chimney-valance, wool and silk, warp-thread of linen; 27 x 184 cm., North-Netherlands, second part of the 17th century.

Cat. nr. 29.

Owner: Rijksmuseum, Amsterdam Inv. nr. 16495/B).

28. Chimney-valance, wool and silk, warp-thread of linen; 30 x 327 cm., North-Netherlands, middle of the 17th century, Cat. nr. 30.

Owner: Koninklijke Musea voor Kunst en Geschiedenis, Brussels (inv. nr. 3379).

29. Bed-spread (?), wool and silk, warp-thread of wool.

268 x 265 cm., Delft, Aert Spiering (ca. 1593-1640) - 1626.

Owner: H.M. The King of Sweden (inv. nr. HGK 423).

30. Back of a chair of walnut, covered with tapestry, warp-thread of linen. North-Netherlands, first part of the 17th century.

Cat. nr. 33.

Owner: Private property.

31. Seat of the chair nr. 30, warp-thread of wool.

32. Chair of walnut, covered with tapestry, wool and silk, warp-thread of linen, North-Netherlands, middle of the 17th century.

Cat. nr. 34 a + b.

Owner: Regenten van het "Deutzenhofje", Amsterdam.

33. Chair of walnut, covered with tapestry, wool and silk, warp-thread of linen. North-Netherlands, Delft (?). Maximiliaan van der Gucht (?) 1663 (?). Probably one of the fourteen chairs supplied to the City of Delft by Maximiliaan van der Gucht in 1663 (3). Cat. nr. 35.

Owner: Stedelijk Museum "Het Prinsenhof", Delft.

34. Item nr. 33. A second chair.

35. Elbow-chair, covered with tapestry, warp-thread of linen; North-Netherlands, Gouda(?). Second part of the 17th century.

Cat. nr. 36.

Owner: Stedelijk Museum "Het Catharina Gasthuis", Gouda (20.271).

75/10/3-6

36. Back and seat of a chair, wool and silk, warp-thread of linen; North-Netherlands, middle of the 17th century. Cat. nr. 38.
Owner: Rijksmuseum, Amsterdam.

37. Tapestry, wool and silk, warp-thread of wool; 245 x 195 cm., North-Netherlands, Delft (?). Workshop of Frans Spiering (?) or Aert Spiering (?). End of the 16th or first quarter of the 17th century. Cat. nr. 41.
Owner: Rijksmuseum, Amsterdam (1967-25).

38. Tapestry, wool and silk, warp-thread of linen; 245 x 200 cm., North-Netherlands, Delft(?), first part of the 17th century. Cat. nr. 42.
Owner: Rijksmuseum, Amsterdam (inv. nr. NM 1999).

39. Tapestry, wool and silk, warp-thread of wool; 246 x 192 cm., North-Netherlands, first part of the 17th century, Cat. nr. 43.
Owner: Private property.

40. Tapestry, wool and silk, warp-thread of linen; 240 x 210 cm., North-Netherlands, beginning of the 17th century. Cat. nr. 44.
Owner: Rijksmuseum "Muiderslot" (on loan from the Rijksmuseum, Amsterdam. (16439)).

41. Table-cloth, wool and silk, warp-thread of wool; 270x 260 cm., Brussels, François Van den Hecke, middle of the 17th century. Cat. nr. 49.
Owner: Rijksmuseum, Amsterdam.

42. Table-cloth, wool and silk, warp-thread of wool; 236 x 188 cm., North-Netherlands, before 1671. Cat. nr. 54.
Owner: Frederiksborg Slot, Denmark.

43. Cushion in tapestry technique, warp-thread of wool. "The story of Jacob", North-Netherlands, middle of the 17th century.
Owner: Rijksmuseum, Amsterdam.

44. Cushion in tapestry technique, warp-thread of wool. "Jacob struggling with the Angel", North-Netherlands, middle of the 17th century.
Owner: Rijksmuseum, Amsterdam.

45. Table-cloth, wool and silk, 169 x 260 cm., North-Netherlands, third quarter of the 17th century. Cat. nr. 58.
Owner: Nijstad Antiquairs N.V. 's-Gravenhage.

RESULTS

In the analysis of the dyestuffs of the tapestries there were not many problems. Only in a few cases the dyestuff could not be analysed. Although the table-cloths are rich in range of colours, the dyestuffs used to achieve this range were limited. The following dyestuffs could be analysed: Cochineal, madder, Brazilwood, and some other redwoods, weld, fustic, young fustic, dyer's broom, and indigo or woad. Table I shows the results of the analyses. No kermes was found in any of the tapestries, which is in accordance with data obtained from research on red dyestuffs from the period 1450 - 1600 (5). This research has shown that hardly any kermes was used after 1600.

In the table-cloths no archil could be analysed, although in literature (7, 8, 9) the use of archil is mentioned. Especially in tapestries done by Spiering there are often large parts which are light blue or almost colourless at the facing side and bright violet at the reverse. Experiments in the laboratory have shown that after having been exposed to direct sunlight during one month, archil faded completely. After this no archil was found. Thus the absence of archil in the objects examined could be easily explained. In the tapestries nrs. 5, 6, 10, 12, 32, 36 and 40 this in fact could be seen, but the presence of archil could not be analysed with certainty.

The beautiful colour range of the tapestries was achieved by mixing various dyestuffs. Mixtures of two and three dyestuffs are very common, even mixtures of four dyestuffs occur. All the mixtures we found are shown in Table II.

Blue

All the blue shades were dyed with indigo or woad. No distinction could be made between these two dyestuffs because they are chemically identical. More research should be done to make identification feasible, possibly through a study of the admixtures of these two dyestuffs separately.

Green

The green shades were in all cases obtained by dyeing the wool or silk first with indigo or woad and after that with a yellow dyestuff. Only two yellow dyestuffs were used for this purpose, weld and dyer's broom. Both were used in about 50% of all the green samples. In literature (7, 8) dyer's broom is often mentioned as the dyestuff used for mixtures with indigo to achieve green colours, because dyer's broom has a greenish yellow colour of its own and is therefore not that suitable as a pure yellow. The light-fastness of dyer's broom is less than that of weld (10). Owing to this bad light-fastness original green parts of the tapestries are nowadays blueish because the yellow dye has faded out.

75/10/3-8

Orange

In about 90% of all pure orange shades madder has been used as the principle dyestuff. In almost 60% of the samples madder is combined with dyer's broom. The other yellow dyes used are: weld and young fustic, the latter only in tapestries nrs. 2, 28, 37 and 39. Between the orange shades one can also range a more brownish shade. This shade is in about 90% dyed with Brazilwood. However, the colour was originally more red because Brazilwood is slightly blueish red. We could establish that Brazilwood fades into a brownish red colour.

Yellow

In almost 80% of the samples weld was used. For silk weld was employed exclusively. Fustic and young fustic were used only very rarely. When dyer's broom was present the colour was more greenish.

Red

In the red shades a rich scala of mixtures was found. Mixtures of e.g. madder, cochineal and Brazilwood were very frequent. In contradistinction to the dates found in the research about red dyestuffs (5) cochineal has been used for dyeing wool as well as for silk. When pure cochineal was used the shade became more violet red (scarlet). In only one tapestry, nr. 26, cochineal was dyed on a mordant of an iron salt, which gives a bright, very fast violet colour. Where madder was used purely the shade turned more brick-red.

An interesting point is the presence of what we have called the "unknown red spot". In many tapestries there are mixtures of e.g. cochineal, madder and Brazilwood or weld. The chromatograms of these mixtures show below the spot of purpurin a small red spot. Because madder is present in all mixtures there is a chance that the spot originates from a third component present in some qualities of madder. In the near future we will try to isolate this component from the thin-layer plate and identify it by means of infra-red spectrometry and other methods. At this very moment we use the "red spot" as an aid in the division of the tapestries into groups.

Another interesting aspect is the presence in some tapestries of purpurin. Madder contains equal quantities of alizarin and purpurin. The colour of the samples in which only purpurin could be analysed is rose-red. The light-fastness of this colour is very bad. Hence this colour remained on the reverse of tapestries a bright rose-red and has faded on the facing side. This was observed quite clearly on tapestry nr. 38: one thread of about 1.5 cm. had all colour shades from bright rose-red to nearly colourless. This thread we cut into five pieces and each part was analysed separately. The chromatograms showed the fading of purpurin very clearly. An explanation for the presence of purpurin with the absence of alizarin is not easily found. Possibly a different varie-

ty of madder has been employed. There is an Indian variety of madder, Munjeet, which contains only purpurin (12). However, commercial traffic between India and Holland was not very frequent in the 17th century. Moreover, it is known that the best quality of madder came from Zeeland, a province in the southwest of Holland (11), so the Dutch dyers did not have to go far out of their way to obtain a product perfectly suitable to their trade.

A second possibility lies in the circumstance that purpurin is soluble in cold water, whereas alizarin is not. If use has been made of this property it could point to a special workshop technique. The preparation can be done in two ways. It is known that the solubility of purpurin in water at a low temperature is much higher than that of alizarin, whereas alizarin dyes fast at a lower temperature than purpurin.

Experiments were carried out to determine if it is possible to isolate purpurin from raw madder by cold extraction. The experiments are taken at temperatures between 30°C. and 95°C., with an interval of 10°C. The extracts are chromatographed in order to find out if alizarin and purpurin are both present. From the chromatograms it could be deducted that purpurin is extracted below 50°C. The extracts are used to dye new wool and of this samples are taken and prepared as usual, so that the dyestuffs can be analysed. Chromatograms of these samples show that it is possible to dye with purpurin only when madder is extracted with water below about 40°C. The colour obtained in this manner is indeed rose-red. Although the preparation of purpurin following the above-mentioned method is possible, it requires a good knowledge of dyestuffs and of the process of dyeing. It is possible that this process was practised in some workshops.

A problem in the interpretation of the results is that it is not at all clear whether the yarns were dyed by the weaver or by a professional dyer(3). On this aspect more research in archives should be done.

CONCLUSION

Through identification of particular mixtures of dyestuffs we hoped to discern in the "Woven Bouquet" tapestries certain groups which could be traced to their place of manufacture. But we did not succeed. The various particularities in dyeing methods, e.g. with "red spot", young fustic and purpurin appear to have been common to all specimens. There are a few tapestries of which the weaver or the place of manufacture are known, but these data cannot be correlated with particular combinations of dyestuffs. However, in spite of this disappointment we did learn much about dyes and dyeing processes in 17th-century Holland.

ACKNOWLEDGEMENT

The author is very grateful to the owners and custodians of tablecloths who gave us permission to take samples from the objects under their protection. Without cooperation from the Rijksmuseum in Amsterdam, especially from mr. C.A. Burgers and mr. H.S. Bloedhouwer, our research could not have been carried out. The practical chromatographic work was carried out by miss W.G.Th. Roelofs. Without her unending patience and perseverance this study could not have been done successfully.

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A B S T R A C T

Dutch flowered tapestries of the 17th century are very famous. They are brilliant in colour. About 50 to 60 specimens of the total production of tapestries remained preserved. From almost all tapestries samples could be taken for dyestuff analysis. The tapestries were made in Gouda and Delft, but it is not clear in which of these two towns each single tapestry originated. A research was done to determine if it is possible to divide the tapestries in groups of the town of origin. However, we did not succeed. Yet, much information was gathered about the process of dyeing and dyestuffs used in Holland in the 17th century. For example twenty eight different combinations of red dyestuffs were found.

75/10/3-12

Note to the Tables: In order to make a clear survey of the results of analysis possible, all dyestuffs found in the tapestries studied are numbered from I to X (Table 1) and all red shades from A to Z² (Table II).

- I = Madder
- II = Cochineal
- III = Brazilwood
- IV = Redwood
- V = Weld
- VI = Young fustic
- VII = Dyer's broom
- VIII = Indigo or Woad
- IX = Red spot, unidentified red dyestuff
- X = Archil ?

- A = cochineal
- B = madder
- C = purpurin
- D = madder + cochineal
- E = madder + brazil
- F = madder + cochineal + brazil
- G = madder + redwood
- H = madder + archil ?
- I = madder + dyer's broom
- J = madder + dyer's broom + young fustic
- K = purpurin + brazil
- L = cochineal + redwood
- M = madder + "red spot"
- N = madder + brazil + "red spot"
- O = madder + redwood + "red spot"
- P = madder + brazil + dyer's broom + "red spot"
- Q = madder + brazil + cochineal + "red spot"
- R = madder + dyer's broom + "red spot"
- S = madder + young fustic + "red spot"
- T = cochineal + brazil + "red spot"
- U = madder + cochineal + "red spot"
- V = madder + brazil + weld
- W = madder + brazil + cochineal + weld
- X = madder + weld
- Y = redwood
- Z = archil
- Z¹ = brazil
- Z² = brazil + dyer's broom

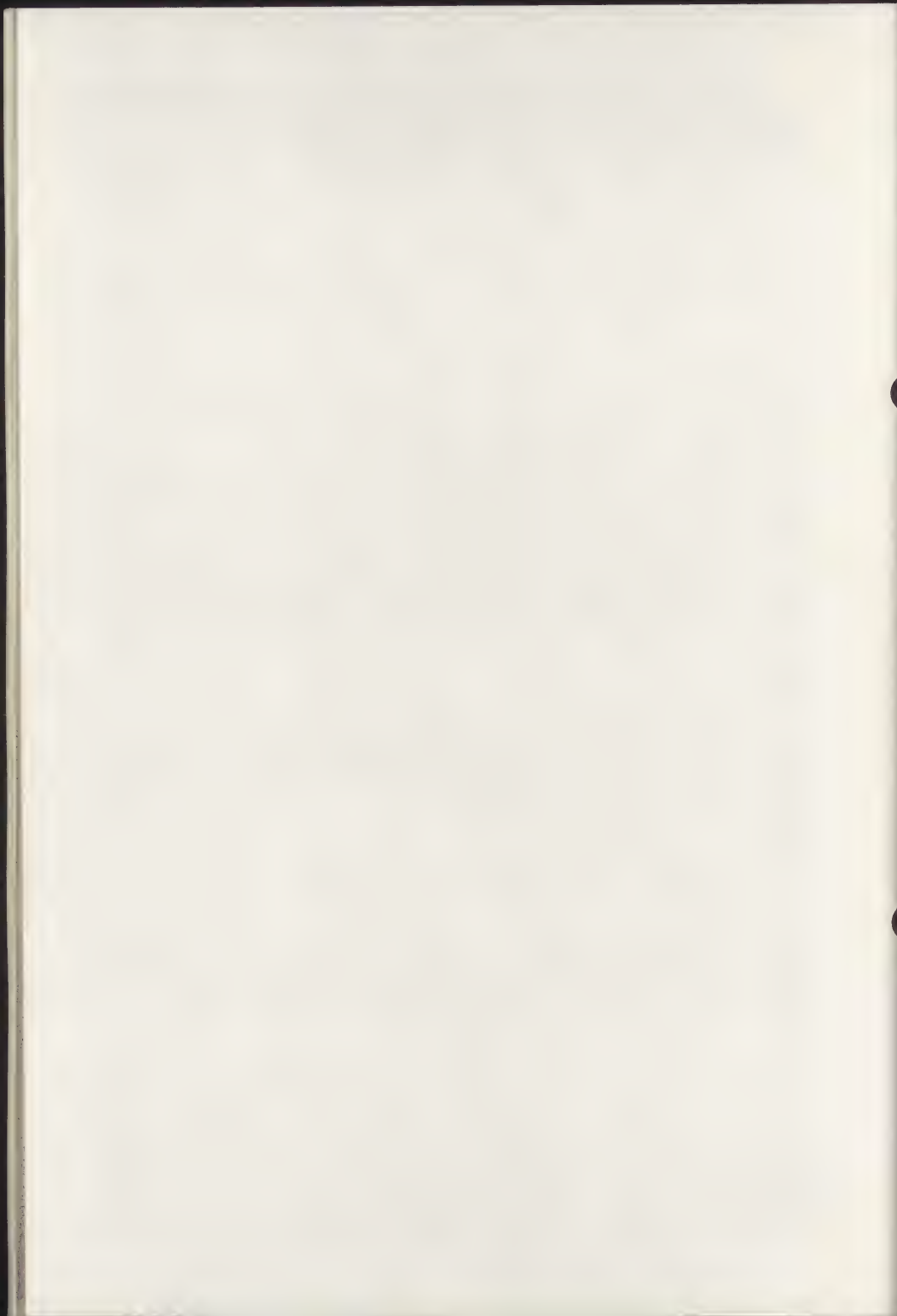
Table 1: Dyes found in the tapestries

	I	II	III	IV	V	VI	VII	VIII	IX	X
1	+	+	+		+			+		
2	+	+			+	+	+	+	+	
3	+		+		+			+		
4	+	+	+		+	+		+	+	
5	+		+	+	+		+	+		+
6	+	+	+		+			+		+
7	+	+	+		+			+		
8	+	+			+			+		
9	+	+	+		+		+	+	+	
10	+	+		+	+		+	+		+
11	+	+	+				+	+		
12	+	+	+				+	+	+	+
13	+	+			+		+	+		
14	+	+			+			+		
15	+	+	+	+	+		+	+		
16	+	+	+		+		+	+		
17	+	+	+		+			+		
18	+		+				+	+		
19	+	+	+		+		+	+		
20	+	+	+		+		+	+		
21	+	+	+		+		+	+	+	
22	+						+	+		
23	+	+			+		+	+	+	
24	+	+	+		+		+	+	+	
25	+	+			+		+	+	+	
26	+	+	+		+		+	+	+	
27	+		+		+			+	+	
28	+	+			+	+	+	+		
29	+	+	+		+		+	+	+	
30	+		+				+	+	+	
31	+		+		+		+	+	+	
32	+	+	+	+	+		+	+		+
33	+				+		+	+		
34	+			+	+			+		
35	+	+		+	+		+	+		
36	+	+		+	+		+	+	+	+
37	+				+	+	+	+	+	
38	+	+			+		+	+	+	
39	+		+		+	+	+	+	+	
40	+	+	+		+		+	+	+	+
41	+	+	+		+		+	+	+	
42	+		+		+		+	+		
43	+		+	+	+		+	+	+	
44	+	+	+		+		+	+	+	
45	+	+	+		+		+	+	+	



Table II: Red shades found in the tapestries

	O	P	Q	R	S	T	U	V	W	X	Y	Z	Z ¹	Z ²
1								+	+	+				
2				+						+				
3														
4					+									
5											+	+		
6												+		
7										+				
8														
9				+								+		
10														
11														
12												+		
13														
14														
15													+	
16													+	
17														
18														
19														
20								+						
21														
22														
23							+							
24						+							+	
25														
26														
27													+	
28														
29													+	+
30				+									+	
31		+												
32												+		
33														
34														
35														
36	+												+	
37														
38														
39														
40												+		
41				+		+							+	
42										+				+
43		+									+			+
44						+							+	
45			+							+			+	



INVESTIGATIONS OF ARCHAEOLOGICAL TEXTILE AND RESTORATION OF THEIR DECORATION

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VChNRTs

USSR

Textile, which go back from ancient times and discovered by archaeologists when excavating ancient burials, are usually destroyed and damaged. These damages are caused by effects of salts from soil, products of desintegration of organic substances, presence of metallic objects. Textile when being in soil for a long time change, discolour, become fragile, loose strength and are destroyed when touching. The remaining cloths are glued under gumin acid effect when converting into strata mass.

Though even in these conditions textile give us enough information about kind of fibres and a way of spinning; about dyes with which their fibres have been dyed. The traces of dissappeared mettalic ornaments, pearls, glass beads, etc. and elements of ornament drawing and peculiarities of seams.

The task is that on the basis of this information discovered by means of modern methods of investigation have taken scientific idea of original state of textile and fabrics of it.

The work on study textile under excavation usually begins in laboratory conditions, i.e. when textile was damaged with taking off burials. That is why it is important from the very beginning - in the field conditions - to take textile from the burials without damages as possible, without causing supplementary mechanical damages of materials, without changing their chemical structure.

In All-Russian artistic scientific-restoration centre after Grabar (VChNRTs) particular method on taking off archaeological cloths from skelette in the process of excavations. This method permits us to separate cloth from skelette without damages, and separate different layers of cloth, to find out the form of ancient cloth.

To take off, clean and stretch cloth neutral organic solvents and pure glycerine without water are used due to it textile preserve its form and sizes, chemical structure of their fibres and dyes isn't deteriorated.

To study dyes of ancient textile in VChNRTs a way of comparative luminiscence characteristics worked out in 1967 E.Phedorovitch is used (Institute of Languages of AS of Uzb. SSR) and a number of other ways.

Ornaments on textile, visible colour of which has been lost are discovered by particular kinds of photography in reflected infra-red rays and due to luminiscence of dyes in ultra-violet rays. This photography helps one to restore invisible outline of decoration. Then on the basis of analysis of dyes original coloration of textile is restored.

Early unknown decoration of some medieval textile were restored. In 1971 in the upper reaches of Don medieval burial of warrior-nomad has been discovered in which the remains of his cloth were found. He ^{was} put into

caftan of decorated silk, into iron chain armour; there is a helmet and a sword near him. Chain armour reached up to thigh, and hands were covered up to elbows.

As a result of effects of products of iron decay textile was preserved in fragments on the right: a part of sleeve up to elbow and fragments of caftan, woven with gold-spinned band.

Fragments of textile darkened, became fragile, lost their strength. To separate sleeve from the lower part of caftan made it impossible. By means of particular impregnation one succeeded in separating the sleeve from skirt, and then taking off skirt from skelette. By insoluble solvents pollutions were removed from textile; then fragment have been stretched and relined.

Analysis of dyes showed that textile was embroidered with yellow and red decorations on blue phone. Visible blue indigo looked like black on the silk under products of ferrous; yellow dye converted into dark-brown; red colour of silk (marena) darkened and was almost invisible. Luminiscence of dyes in ultra-violet rays are not absolutely observed.

Analysis of dyes permitted one to choose a way of removing ferrous products. As a result of treatment textile became soft, dissappeared friggility; colours of decoration before invisible appeared.

Decoration of textile was discovered due to luminiscence of three dyes in ultra-violet rays.

Owing to work the above mentioned we succeeded in restoring ornaments. Ornament one more of arab textile of XII-XIII cc. was known. May be, it has been made in Sicily. There is a scene of fighting of two birds which is characteristic of arab textile (compositional scheme) and image of human mask among vegetable decoration.

Kiev archaeologists have discovered the burial of rich nomad-polovets. His cloth has been woven from 4 various decorative silk textile of XI c. There were many fragments of this textile. This textile was comparatively strengthened, but discoloured completely. Only ornaments embroidered with blue silk dyed with indigo were differred.

Cloth of warrior consisted of short upper part, as jacket with long sleeves, decorated with rectangular textile with traces of weaving by green glass beads. Collar sewed to breast-plate was sewed of swatch of the third textile and decorated by triangular silver plates with chased decoration.

Breeches of nomad were sewed of the fourth byzantium textile.

Collar of swatch of decorative silk with the picture of peacocks preserved only trace of blue dyeing of threads. Chervets phone of ornament and yellow out-line of blue decoration dissappeared.

Dyes were determined according to method of Phedorovitch-Kononov. Drawing of decoration was restored due to photography with colour filters. When taking photographs in reflected infra-red rays traces of oxides of silver were observed. These are traces from triangular silver plates sewed whenever. There must be 22 plates, but only nine plates preserved. Thus, a way of decoration of collar is established. On the basis of determining the dyes - chervets (*Porphirophora hameli*), indigo and yellow strengthened dye of vegetable nature appeared to be possible to restore colour of decoration of textile.

Collar is maintained to be sewed of two swatches of precious textile of XI c. Known arab cicily textile is

analogous to this textile. The former is kept in Barse-lona. Composition of the last one is reminiscence of bysantium original which didn't go back up to present. It is possible that nomad textile which collar is made of is the bysantium ancestor of this decoration which is unknown earlier.

Study of rectangular textile decorating the chest of nomad showed that it is a fragment of bysantium silk textile.

Only two glass beads were preserved from embroiding. One succeeded in restoring the decoration due to pinctures. Decoration on textile wasn't visible, only in some places there remained traces of decorations made with blue silk. Luminiscence of dyes in ultra-violet rays are not observed.

After removing ferrous pollutions luminiscence was observed, invisible earlier parts of decoration appeared, negative image of decoration appeared on the back side of textile. All of this made it possible to restore decoration though great damages of face of textile.

The traces of dyeing the silk with chervets in those places where textile was dyed in brown colour have been discovered with analysis of dyes. Blue decorations are formed by threads dyed with indigo.

As a result of reconstruction fragment under study is maintained to be a part of composition of bysantium decorative silk textile with eagles. Such a textile is kept in riznitsa of cathedral in Bricksen. The eagles of blue colour were embroidered on raspberry-red phone (chervets), on bricksen textile as we know due to drawings. One variant of this decoration was shown on the fragment of textile under excavation - there is a raspberry-red eagle on blue phone.

The upper part of cloth of nomad is the most significant material to study. There are many fragments in good state of large sizes. The decoration of textile look like two-colour when daylight: golden lines of ornaments on greenish blue phone.

Ultra-violet luminiscence is distinctly divided two kinds of dyes in outline of decoration. Light outline of decoration were embroidered with silk dyed with mare-na into light-orange colour. In accents silk is dyed with bright-yellow dye - kurkuma, which brightly luminiscented. Phone of textile is blue; for inner parts of decoration is used blue silk of more dense colour.

Study of technology of weaving help us to restore ornaments where colours are damaged and there is no luminiscence in ultra-violet rays. When taking photographs these lines became more distinct. Combinating of these grooves on photos gives an outline of disappeared decoration.

Restoration of textile composition, combined of mosaics of fragments gives an idea of bysantium textile of XI c. which is unknown earlier.

Composition consists of enormous rings, plendously decorated into 4 colours. Diametr of ring is 76 cm. Rings are touched and binded with medalions. There is a rosette with splendid vegetable decoration among the rings. Inside of the rings winged beasts are pictured, preserved in fragments unfortunately.

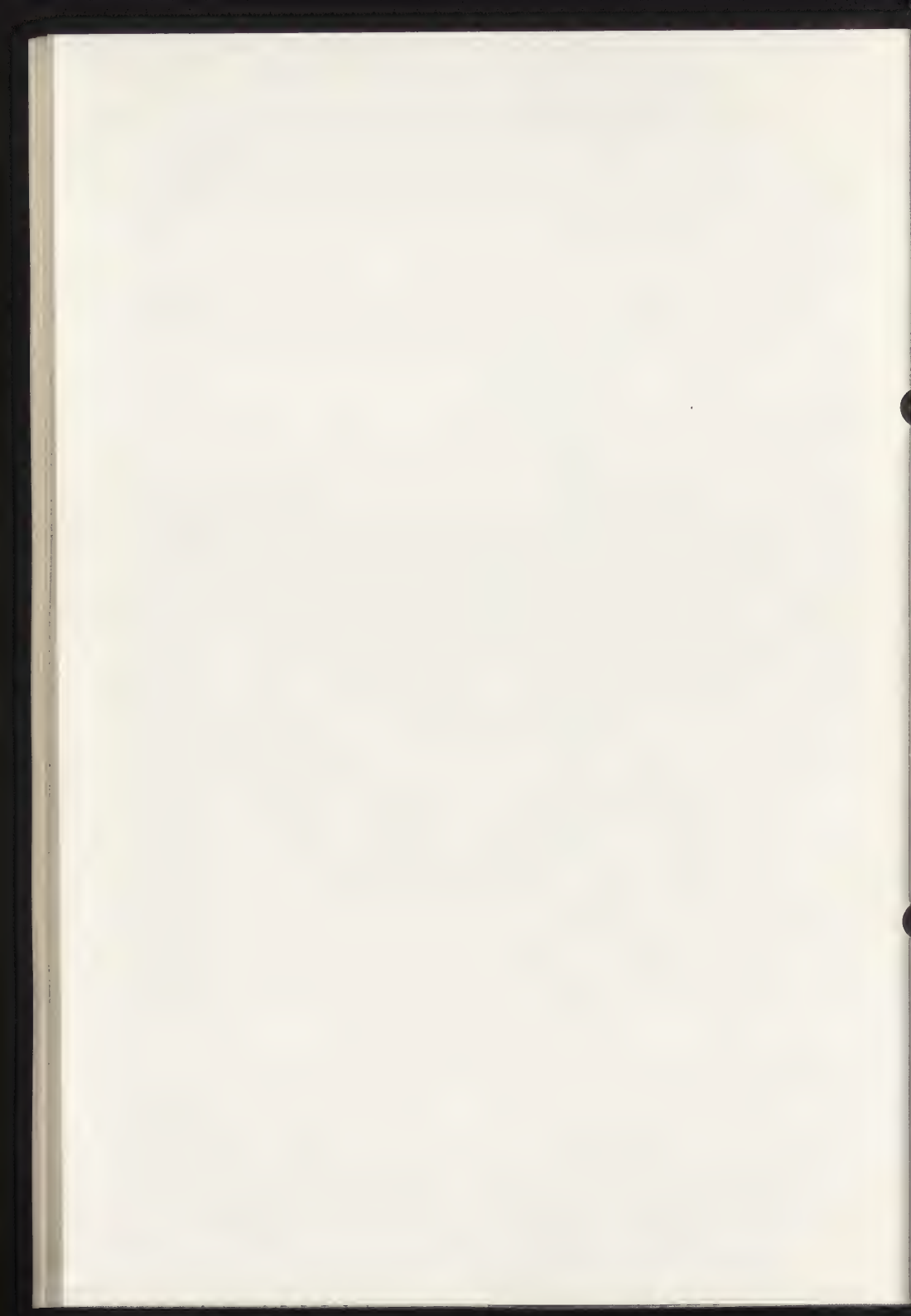
There are visible traces of blue dyeing of silk on the textile of breeches such as on other three textile from the same burial. The back side of textile has negative decoration. Photography in reflected infra-red rays helped one to restore delicate decoration. One succeded in observing the grooves more distinctly in

the places of alternating the colour weaths. Existence of three dyes (chervets, indigo and yellow tanned dye) was established by means of analysis in the outline of decoration.

Large-scale composition with sizes 30x80 cm has been almost completely restored from small amount of fragments of this textile, due to fact that decoration consists of narrow and long bands of decoration which alternates in mirror reflection.

There are embroidered griffons, peacocks, vegetable motifs with bunch of grapes and vases on the textile. Phone of textile is of raspberry colour; decoration is of blue colour with yellow out-line.

Scales of composition, personages and subjects of pictures, use of precious dyes show that fragments under study belong to the most precious silks which were produced in Bysantium in XI c. Precious textile of cloth of nomad may be suggested to be his spoils of war.



DYEING RELINED TEXTILE AND ANALYSIS OF ANCIENT DYES
(PIGMENTS) IN DEPARTMENT OF APPLIED ART OF VChNRTS AFTER
GRABAR IN MOSCOW

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When dyeing textiles used to reline old textile fabrics and repair damages it is very difficult if possible at all, to reproduce ancient colours of textile with modern synthetic dyes.

The cause is in the fact that vegetable dyes applied by ancient masters to dye contain not only isolated dyes, but their mixtures, giving complicated tones of colour. Besides that tinctorial strength of natural dyes can't be compared to dyeing of the same colour obtained by combination of some synthetic dyes.

That is why since 1967 only natural organic dyes corresponding to that of used in original works, have been applying in VChNRTs to dye relined textile fabrics. The exception are only some vat synthetic dyes used to imitate dyeings with ancient natural dyes which are rarely occurred at present.

Some ways which are used by ancient masters to dye textile had been introduce into practice of VChNRTs. All the recipes of old dyeing are taken from vast special literature of the late of XVIII - middle of XIX ,

where an experience of masters-dyers of Russia, Central Asia and european countries has been gathered. Broths of vegetable dyes (bark, roots, dry herbes) are mainly used to dye natural textile fibres.

Natural vegetable dyes belong to mordant dyes. To fix the colours on the materials under dye with vegetable dyes it is necessary to treat the materials with mordants before and after dyeing. Due to this procedure strengthened insoluble compounds called as colour varnishes are formed. Varnishes depending on mordant can convert their colours differed from the colour of initial vegetable dye. For example, the basic dye of marena (*Rubia tinctoria*) - alizarin of orange colour forms depending on nature of metal red varnishes when aluminokalium mordant used, violet varnishes when ferrum mordant used, brown varnishes when cuprous mordant used.

Since the 1971 every year seminars on methods of dyeing with natural organic dyes and mordants^{has being held}. Textile restorers from many restoration laboratories of Soviet Union take part in the work of these seminars. These seminars are under guidance of the authors of the report. When seminars are over all the participants are given home task and by the next seminar they show their dyeings of relined textiles.

Albums of standard dyeings which are compiled in every restoration laboratory consist of textile swatches dyed with vegetable dyes into all-possible tones obtained by using various mordants. More than 20 vegetable dyes are tested when 6-8 mordants used. Thus, textile restorers gain an idea of all the wealth of colour which may be obtained from each plant by means of combination of mordants and master ways of dyeing.

At present participants of seminars on dyeing can reproduce wide range of textile dyeing by such ways and materials which are used when dyeing the ancient textile. Program of seminars includes obligatory training in vat dyeing with indigo-natural and artificial dye. Beside that dyeing by some artificial indigo-dyes which are able to imitate such rare ancient dyes as koshenil, safflower, orlean, chervets (at present it is difficult to obtain them).

Simultaneously with training in dyeing with natural organic dyes restorers mastered in indentifying the dyes on museum textiles.

To investigate the dyes of ancient textiles an approach worked out by the author of the report Eugenia Phedorovitch (Instituted of Art AS UzbSSR) in 1967 is used.

The essence of approach called as "way of comparative luminiscent characteristics" is in comparison of visible colour of the fibres under investigation and their luminiscence, excited by ultra-violet rays before and after treatment of it with 2 percent HCl with the colour of standard dyeings, regarded in the same conditions. Each standard consists of two parts: standard dyeing with natural organic dye and any mordant, treated by boiling of it in 2 per cent solution of HCl.

The first part of standard contains varnish of a dye under study on the textile; in the second part of standard varnish has been decayed and these remain free dyed and tanned substances and the products of their conversion under acid effect as well.

Both parts are of different colours under daylight. Ultra-violet luminiscence of the same parts provides with two colour characteristics more of dye under study.

According to experiments of the author of the method its own combination of four colour characteristics precisely corresponds to each kind of dyeing raw materials. On this basis identification maps with colour standards to identify the kinds of raw materials applied in Central Asia are prepared by the author. The experiments on making the same standards for european ways of dyeing is being carried out in VChNRTs and State Hermitage Museum.

To find out the possibilities and the limits of using this method further investigations and making the standards on all kinds of raw materials are necessary, at present application of this method essentially enriches practice of scientific textile research. Kinds of dyeing raw materials differ from each other enough distinctly. It is obvious particularly in the case of similar tanned substances as busgyng (galls of phistashio) and bark of granate. When forming on fibres varnishes of these dyes with ferrous mordant luminiscentes in various way. Various luminiscence is showed by free tanned substances of these dyes.

Colour characteristic of such similar dyes as iran kermes, chervets (*Porphiro-phora hameli* Brand) and mexicanian koshenil (*Dactilopius cacti* L.), which have similar colour reaction when analyzing with chemical agents.

Various combinations of 4 colours are formed with two kind of marena dyeing - european (*Rubia tinctoria*) and oriental (*Rubia cordifolia*).

The way of comparative luminiscence characteristics is suitable for identification of kinds of dyeing raw materials of which textile archeological and ethnographical of any colour are made. This way is of great im-

portance to examine fibres of yellow, green and black colours dyed with dyed plants containing flavons, antra-derivates and tanned substances ways of identification for which have not been worked out. Various plants dyeing in these colours occur in flora of each country and the necessity to import them was the least one due to this fact.

In this case identification of dyes gives a possibility to determine the genesis of the textile according their colour.

By this way mixtures of dyed plants are discovered well. It is essentially to examine green and violet fibres. Kinds of dyed raw materials with which red fibres were dyed are discovered more exactly in this way than the others.

The investigation of colours of archeological material is complicated in particular. Here we use combined methodics - "wedge of Kononov", colour reactions, way of comparative luminiscence characteristics the above mentioned and a number of other ways known.

To investigate of colours preserved on the textile one begins to determine colour reactions on the fibres; then dyes are extracted from textile by ways corresponding to the nature of dye and technology of dyeing the textile.

The extraction of dyes from small amount of materials under study is carried on according method worked out by science worker of State Hermitage Museums Vasilij Kononov. This method is a variety of paper chromatography and is as the following: chromatography or filter paper strips cut as a wedge in lower part are soaked in ether extract of dye. When the solution reached the middle of a wedge, the last one is quickly removed from

the solution and dried. The procedure is repeated many times to accumulate dyes on a wedge. Then a wedge with dyes extracted is soaked in pure acetato-ethyl ether; when soaking dyes are separated on a wedge. Bands of individual dyes appear on a paper. Then extracted dyes are indentified according the method of comparative luminiscence characteristics and colour reactions.

It is comfortable to extract the traces of dyes from desintegrated or carbonized archeological textile and to use this method when these is small amount of material under study.

Application of methods the above mentioned to study the dyes of ancient textile gives the possibility to restore the decoration of textile unknown before and found when excavating the medieval burials of nomads on the territory of Russia and Ukraine - four kinds of bysantium textiles of XI c, arab textile of XII-XIII cc. and chinese textile of XII c.

The dyes from textile and traces of leather from rich burial of sarmathian woman have been extracted and identified by methods of Kononov and Phedorovitch (2 B.C.). Only remains of felt which a bag to keep cosmetics is made of preserved visible colours with chervets (iran kermes - *Rorphirophora hameli*; Brand).

Fragments of two other textile - the thinnest silk muslin and dense reps textile of silk have brown colour, typical for archeological finds of such kind.

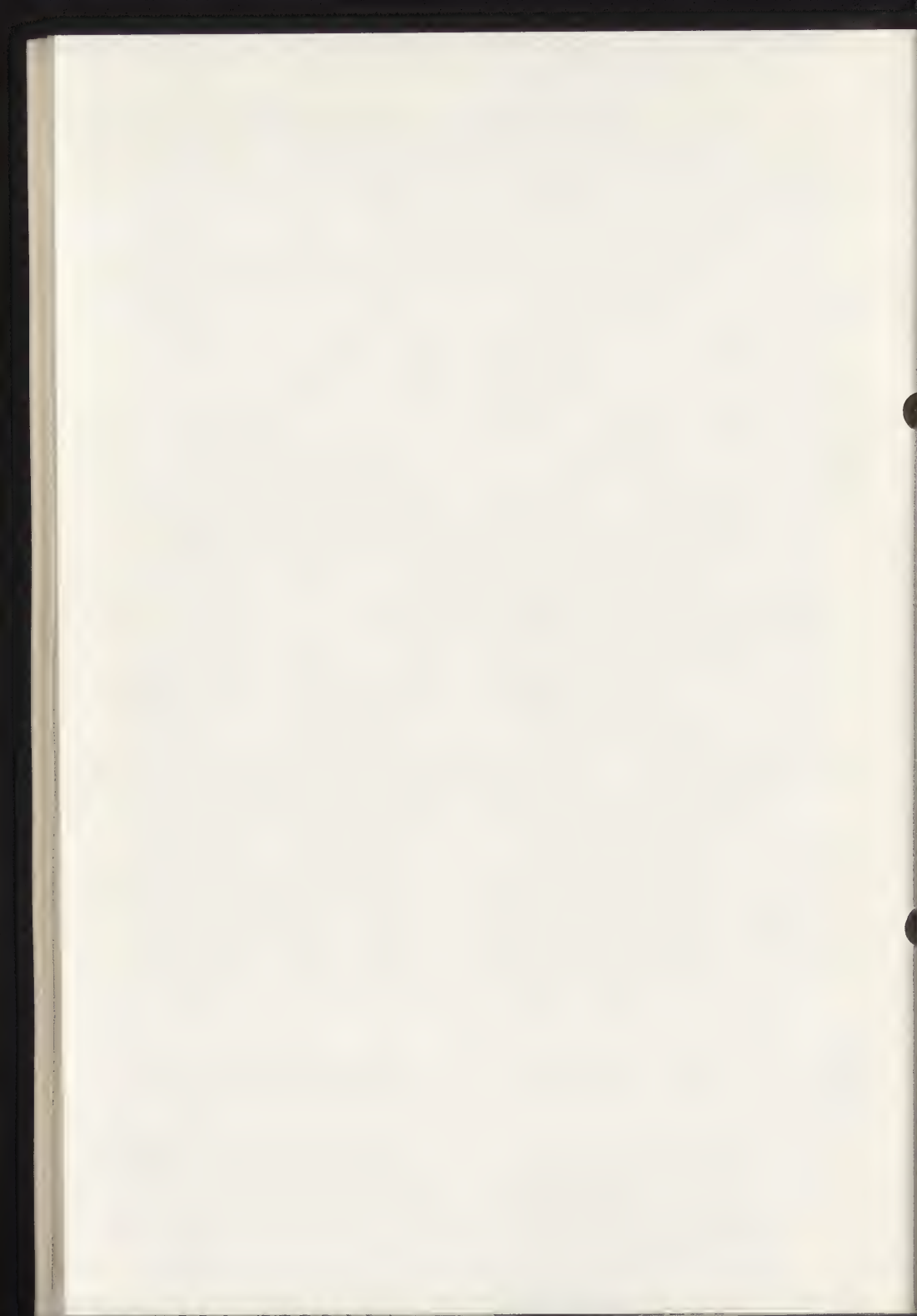
Pink dye - saflor (*Carthamus tinctorius* L.) which one succeeded in extracting from silk of thin muslin covering without visible colour is extracted by means of wedge of Kononov. Traces of dyeing with marena were extracted of fragments of reps textile.

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From the remaining decayed then leather with the traces of sewing by means of the oldest spinned gold (it is 1000 years older than known gold cyprus threads) purpur has been extracted in its original unchangable appearance.

Pink rouge rubbed with talk and chervets has been discovered in this burial of sarmathian woman.

All the dyes became visible on wedges of Kononov. Bright luminiscence of them illuminated by ultraviolet rays has been discovered. It corresponded to nature of 4 red dyes exactly.



REPORT ON THE GREENWICH LINING CONFERENCE

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ABSTRACT

A short report on the first International Conference on Comparative Picture Lining Techniques, held at the National Maritime Museum, Greenwich, from 22nd to 25th April 1974.

The critical part played by the lining process in the restoration of a painting has hitherto received insufficient attention in the field of conservation research. Until a few years ago paintings were often damaged and the surface diversely affected when a reinforcing canvas was applied to the reverse of the picture canvas. More recent methods involving the use of hot tables and vacuum pressure, and other methods produced since then, have changed traditional lining techniques, but have created a number of related problems and side effects which may still impair the picture's final surface. Fortunately one need only compare one or two of the unlined masterpieces remaining from the seventeenth century (such as the portrait of Philip II by Velasquez in the National Gallery) with the vast majority of other works which have been lined, to see how the surface structures may be changed beyond recognition by the process.

In April 1974, the Picture Restoration Department of the National Maritime Museum (Director, Basil Greenhill), with the substantial support of the museum's education and administrative services, initiated the first International Conference on Comparative Lining Techniques, attempting to reassess the fundamental purposes, and to review current techniques, with the intention of resolving the choice of a particular lining treatment to suit the requirements of individual paintings. The widely differing attitudes to lining, the numerous methods and different materials employed by the various nations and various individual conservators were demonstrated (mainly for the first time ever in public) by delegates from twenty-four countries, in the sympathetic surroundings of the Greenwich Theatre.

To line a painting means to attach a new support to the back of the original painting to give it increased strength. The term 're-lining' means the replacement of a lining and the re-attachment of another further support. Sometimes lining is confused with the transfer of a new canvas to the back of the artist's original paint layer, a delicate operation which had a vogue in the eighteenth and nineteenth centuries, but today lining a painting is usually considered sufficient to strengthen the weaker parts of the support and paint layers.

The natural fibres found in the canvas of many old paintings are remarkably tough and resistant against the effect of deterioration from age, but they are often coated or embedded in glue size or flour-paste or combinations of animal or fish glue, sometimes mixed with humectants such as honey or sugar. These compositions can be attacked readily by micro-organisms, or the mechanical weakening brought about by the changes of climate affecting the canvas, which is subject to a continuous

dimensional change, the frequency of which is regulated by the surrounding climate.

This subsequent weakening of the support for the painting happens predictably in the areas undergoing most stress. These are the upper edge and corners, followed by the upper sides. The eventual breaking away of the canvas in these positions, caused by the dimensional changes and the abrasive effect of the edge of the stretcher rubbing against the canvas, results in a weakening and a final splitting away of the painting from its original stretcher.

One has a choice of three ways to overcome this failure:

1. Strip lining - attaching strips of canvas to the edges of the original canvas and re-stretching the painting on a stretcher.
2. Sticking the painting on to a panel support - for example, marouflaging; this came into common practice in the eighteenth century.
3. Lining - attaching a new canvas to the back of the original painting.

The practice of lining evolved towards the end of the seventeenth century, about 150 years after the introduction of the oil painting on canvas technique. The ever-increasing rate of decay of pictures in the late eighteenth and early nineteenth centuries is reflected in the rise of the number of restorations recorded, and in the wave of interest shown in lining and transfer techniques. The attention of the art world was gripped by the amazing technical feats of transfer carried out in France by Hacquin and Picault. Although almost all of these methods were still based on the use of animal glues and casein, and on marouflage using pigment/oil cements, the first experiments with wax, both for lining and for blister-laying, had been carried out in the mid-eighteenth century. But the earliest record of wax as a firmly established lining adhesive is not until 1858, when it was in use by Carbonelle of Brussels for this purpose.

Today the wax impregnation method is in very common use in countries in the Western world. Thousands of paintings have been lined or impregnated by the use of wax or wax-resin mixtures. Not all of the paintings treated have fared well. In some cases, the tonal drop has almost a blackening effect, where the ground or the priming has become considerably darker and thus the colour values of the original painting are sometimes savagely altered.

The dangers of a change in tone of the paint caused by the infusion of wax or wax-resin has only recently been redefined. The rough rule of thumb criteria that oil paintings will take a wax-resin impregnation, while tempera or gouache paintings will not, no longer wholly serves, for some oil paintings are almost as radically changed as tempera paintings by the wax impregnation method. The tragedy of the darkening of the Mantegna Cartoons at Hampton Court can hardly be overlooked in the history of conservation. In 1931, these paintings, executed in a form of tempera on gessoed canvas, were suffused by heavy layers of yellow wax, irreparably bringing a darkening and a lowering of their colour values and paint qualities. The frescoes by Daniel Maclise in the Royal Gallery of the House of Lords were also plunged into darkness by the rash impregnation of beeswax, heated into the surface with blow-lamps. Attempts were even made to impregnate the great Raphael Cartoons in the Victoria and Albert Museum, painted in tempera on paper. The rapid darkening of the painting, where the paper turned dark brown, was only checked by the sharp intervention of a youthful restorer who protested that this method was not to be used. This darkened patch remains today; it serves as a useful lesson to all restorers that the choice of adhesive must be matched to the physical and chemical structure of the painting.

In 1930 an international conference on painting conservation met under the aegis of the International Museums Office to discuss these aspects of wax impregnation and lining methods. Ten years later it published an early specification for a hot table, which made it possible to ensure a uniform melting of the adhesive through to the paint surface, thus dispensing with the ironing of the front or the back of the painting, which was often necessary to obtain complete adhesion.

The increasing confidence in the wax resin/hot table method brought about another innovation in picture conservation technology. This was the introduction in 1955, by R E Straub and Stephen Rees Jones, of the vacuum principle in connection with the table.

To carry out a successful lining on a vacuum/hot table, using a hot melt adhesive such as wax/resin, is one of the most difficult operations in conservation, if this is to be carried out without the painting taking on characteristics not inherent in its original structure, but imparted as side effects of the method. By 1960, these limitations were recognised and were being officially circulated. In a UNESCO study on fabric paint supports Dr Christian Wolters writes, 'The structure of the canvas, which is so important, is in danger of being altered;

either the grain is pressed out, or on the contrary, it is accentuated; as for instance when the vacuum method is used.' Many of the paintings lined by this vacuum/hot table method between 1955 and 1965 show evidences of this defect.

The battles which restorers faced at this time with the vacuum hot table can, unfortunately, all too often be seen imprinted on the surfaces of the paintings in public galleries. Indeed, the term 'weave imprint' is now recognised as one of the common defects of the system, arising not only from the use of too high a vacuum pressure, but from an as yet irremovable defect inherent in the system whereby the relief and structure of the underlying layers of the painting and lining support are transmitted to the paint surface and held in a compressed state by the hot melt wax adhesive layer during the lining and setting stages.

By about 1965 other ways were being sought to remove these unwanted surface defects which seemed to be inherent in the vacuum method. The vacuum hot table principle, which had been essentially designed for a 'face up' method of lining, where the surface of the painting was protected by the rubber membrane, now came to be also used as a means of producing overall heat for a 'face down' method where the picture lay with its face against the table only separated by a layer of insulating Melinex or a thin rubber buffer. The canvas support lay on top, and the wax lining which followed, fused the original painting and the lining canvas together in as satisfactory a fashion as with the previous method, but eliminated the canvas weave emphasis which had been so apparent with the 'face up' method. Paintings with high impasto or special relief textures could not, of course, be lined in this way, but many pictures with low impasto showed an improved surface, and paintings with tears or small areas of cupping could often be successfully treated. Although this method is now more generally accepted, it was hardly referred to in any of the technical studies. Obviously it was open to severe criticism. The use of additional heat sources such as banks of infra-red bulbs or elements placed above the painting held by vacuum to the hot table partly reduced the problem of heat transmission which previously had to pass through the surface of the paint layers, but it is common to find on paintings lined by the face down method the scars of surface patterns where the facing papers have been pressed into the surface of the paint. By this method the painting could easily be damaged by overheating, but faced with the choice of a pronounced weave emphasis or having a painting where relief was only slightly moated, the restorer would often choose the second course of action.

This conference was the first of a series of three on the subject of painting conservation. Others will be held in due course. It was the natural consequence of the programme of research in picture lining techniques carried out by the National Maritime Museum's Picture Restoration Department.

Among the earlier traditional techniques presented at the meeting, was the beautiful Soviet sturgeon glue hand-lining system, described by Mme. L Jashkina of the Moscow Conservation Laboratory. Other hand lining methods followed, emphasising the care and patience devoted to the techniques by their various practitioners - A.Rothe presented the film of the work of S Taiti and the restorers in the Fortezza da Basso, Florence, in lining with flour paste + animal glue; Philip Robinson, London, described traditional English trade techniques of lining with 'compo' (glue composition paste); and G Messens of the IRPA, Brussels, commented on the film of his own work using natural beeswax + resin to hand line a large painting. The lining techniques of the National Gallery, London, which are based on traditional hand-lining methods were explained by A Lucas; and further problematical wax-resin hand linings, carried out in Poland many years ago, were described and illustrated by the late Prof. B Marconi.

Lining by vacuum hot table was demonstrated live by P Boissonnas of Zurich, in conjunction with hot air blowers, used to melt a new synthetic wax-resin adhesive (Lascaux wax) on woven glass fibre fabric during a face-down treatment on a plastic foam sheet. Vacuum hot table lining was further represented and illustrated in a film made by G Berger in New York of his method using BEVA 371, synthetic resin adhesive + teflon-coated woven glass fibre fabric. Mr Berger also carried out live demonstrations of the application and use of his lining adhesive, both with and without the conventional vacuum lining membrane..

Beeswax-resin adhesives came under a good deal of criticism during discussions (disadvantages having been outlined by me in the introductory talk), but in spite of their drawbacks, they are obviously popular stand-bys for many restorers. Several new and interesting techniques for lining still continued to use them - eg Hedley & Cummings (Courtauld Institute, London) presented a film of a vacuum envelope lining table with an ingenious infra-red traversing heat source, for wax-resin lining; and Mme. Wolska of Poland described her own system of wax-resin lining below a temporary hot water bath, using soft rubber rollers for additional pressure.

Remarkable developments in a direction away from the use of hot-cement type adhesives were presented and demonstrated by V Mehra & J Voskuil of the Central Research Laboratory, Amsterdam, on a prototype cold vacuum lining table, transported specially to the Conference, using Plextol B500 cold setting adhesive. Mr Mehra is presenting the latest version of this technique to this ICOM group. The restorers in the Stockholm Institute for the Technology of Artistic Materials, in conjunction with F Makes, presented a paper on a case-history of consolidation of an old painting, without lining; they were the only speakers to be looking in this direction away from lining altogether. A painting treated in this way was displayed at the Conference exhibition. P Cadorin and M Veillon of the Basel Museum presented a comprehensive survey of case histories of treatments to canvas paintings, illustrating works from a fifteenth century organ case to a canvas by Marc Chagall; in some cases they had completed lining with a pre-fabricated contact adhesive sheet.

In addition to actual lining sequences, many speakers dealt with preparatory treatments before lining. Miss M Watherston, New York, spoke of her experimental work incorporating gentle solvent introduction to distorted paint films, cupping, and crackle, on the hot table under vacuum hold, either before or after lining treatment. This speaker's specific concern is with the conservation of modern paintings. In his film of the work in Brussels, G Messens demonstrated very clearly the importance of correct preparation of the lining fabric, and the means by which he ensures even and adequate stretch before application of the lining adhesive. The audience's surprise at the length of this part of his preparations is perhaps some indication of the lack of attention which is frequently paid to the new lining canvas. David Bull and Robert Shepherd presented a panel of speakers who showed short films on methods of glue removal. Miss J Seddon was working with a light electrical vibrator to remove glue and accretions on backs of canvases in the dry state; Miss G Lewis showed a colloidal clay + water mixture which causes the water to remain in a jelly-like paste on the glue layer, without penetrating the canvas, softening the glue at the same time. J Essex (English liner in commercial practice) presented a film of a vacuum hot table/water based technique for removal of old stubborn glues and linings in one piece, leaving the back of the original canvas in a very fresh state, a most skilful procedure, requiring great care and experience.

The system of prestretching in use in the Greenwich Maritime Museum over the last ten years was also shown on film (described in a paper to this working group in Venice 1975), followed by

the recently developed procedure of lining in a portable vacuum envelope (W Percival-Prescott, R Chittenden, Miss G Lewis).

Testing of materials, and mechanical aspects of lining procedures (still in the early stages in this field) were dealt with by E Tassinari (Italy) in the Physical Characteristics of Canvases, Hedley and Cummings' (Courtauld) experiments with raw canvas on surface texture changes in vacuum lining, and Prof. B Hallstrom's work on the ecology of a painting: microbial deterioration revealed by scanning electron microscope.

During a painting's lifetime, generations of micro-organisms, feeding on the original glue size of the canvas, on the proteinaceous content of some of the paint layers, on subsequent impregnations of animal glue or starch pastes during lining, are born and die inside the picture. They may have been carried in the natural earth pigments used by the painter, or may be air-borne. In time the network of dead organisms that results forms a mechanical barrier to adhesion between the paint layers and the canvas, weakening their attachment. Aided by changes in climate and movement of the canvas support, spontaneous flaking of the paint film regularly occurs.

To date Professor Hallstrom, Director of the Institute of Technology of Artistic Materials and Head of the Art Conservation School of the Royal Swedish Academy of Fine Arts, Stockholm, and his team are the only conservators working on and identifying this aspect of deterioration in paintings.

S Rees-Jones, Head of the Technology Department of the Courtauld Institute, London, summarised his findings from replies to the ICOM Working Group's questionnaire on lining (paper to this meeting also). Throughout the meeting, the chairmen for each session, C Ellison, J Brealey, S Rees-Jones, A Lucas and N Brommelle, who organised the final discussion, encouraged lively audience questioning and participation, which was recorded for inclusion in the final report of the proceedings.

During the evening demonstrations test paintings were lined before packed audiences. Pierre Boissonas of Zurich (Lascaux wax adhesive/woven glass fibre fabric), Vishwa Mehra of Amsterdam (Plextol B500 adhesive/woven polypropylene fabric, on a vacuum cold lining table) and Gustav Berger of New York (BEVA 371 adhesive/woven glass fibre fabric) courageously carried out their full lining procedures. Their finished work was exhibited in the Lining Exhibition Gallery during the meeting, where not only was an extensive range of fabrics, materials and tools from all over the world displayed, but also particular paintings

treated by various lining methods, past and present. Test materials (showing defects and ways to avoid them) from the various centres of lining research were also available for immediate reference.

Assistance on the Conference Committee came from the International Institute for Conservation, the British Council, ICOM, the Association of British Picture Restorers, the Courtauld Institute of Art, a number of distinguished private restorers, and the major London art galleries. The speakers came from all over the world, including the USA, the Soviet Union, Eastern and Western Europe, producing a cross-section of specialists who were very open about their methods; they wrote twenty-three papers in all, covering their approaches to the complicated problems of their work.

Treatments embraced the conservation of old master painting fabrics through to contemporary colour-field works on cotton duck. These papers are currently being edited for grouping together in an extensively illustrated publication by the Conference Committee. Many of the technical films made were produced by the NMM Film Unit at Greenwich and are available on request to me (ICOM Lining Working Group Co-ordinator).

Today, the problems we face are very much the same as those faced by past restorers. They spring firstly from the fundamental weakness of the technique of painting on canvas which is a very expressive but truly impermanent method. Our old enemies, heat, pressure, and the application and absorption of adhesives into paint and support, only lead to the difficulties and dangers of removing these materials, to start once again on the lining cycle. We know that these processes cannot continue indefinitely. Surely one of our most immediate aims should be an attempt to find ways of preventing the need for lining? Some of these ways were described and demonstrated at the Greenwich Conference.

DETRIMENTAL AND IRREVERSIBLE EFFECTS OF WAX IMPREGNATION ON EASEL PAINTINGS

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Fig. 1

The surface of modern paintings is so delicate that it would be marred if touched by a bare hand or rubbed by wrapping paper. A leading gallery keeps them enclosed and labeled as shown above.

Abstract - A painting by Leger utilizing the play of light alternately reflected from mat and glossy surfaces was examined before and after it has been wax-lined. After lining it was no longer the old painting because all its color values were insidiously changed.

Recent research has shown wax impregnation of paintings to be irreversible. Six researchers in Europe and the United States have independently of each other provided objective scientific proof that: 1. Wax stains and discolors many paint films and grounds, 2. Many wax-resin mixtures are prone to discoloration, 3. Wax softens many oil paint films; It makes them soluble in even the mildest solvents; It makes them susceptible to abrasion, 4. Beeswax can cause swelling and cracking of paint films, 5. Wax can never be completely removed once it has impregnated cellulose fibers (canvas, paper, etc.), 6. A wax coating cannot be removed by solvents alone without some mechanical aid such as scrubbing, even if there is no interaction between the wax and the coated material, 7. Wax impregnation prevents the formation of stronger bonds by more effective adhesives.

I. Irreversible Changes in Appearance

A few years ago I was asked to examine a painting by Leger showing a design in glossy black oil paint on a semi-flat white ground. The background, which was filled with a very lean, pastel-like orange-red paint, had several badly restored scratches or tears. Examination revealed this background to be almost powdery, soluble in the mildest petroleum solvents. The condition of the canvas, which was brittle, and the partially cupping paint film prompted me to recommend lining of the painting. Because of the delicate balance of mat and glossy areas and the difficulty of inpainting the flat orange-red background, I asked a rather high price for the restoration of this painting. The owner decided to give the job to another conservator.

Recently I saw the painting exhibited. It had been wax-lined and coated with a synthetic varnish. The mat orange-red background had turned a fiery deep red. The whole painting had the attractive even sheen of a new car or piece of furniture coated with a synthetic polish. There was probably no doubt in the mind of the admiring onlooker-layman that the painting was treated by a careful master conservator capable of turning out a highly finished product. However, it left me with the nagging feeling that Leger himself might not have liked this new version of his painting because he had finished it in an entirely different form.

Could this painting now be brought back to its original condition regardless of cost? I must admit that I would not know how to do it. My notes clearly state that the orange-red background was soluble in mineral spirits. How then would anyone be able to remove the synthetic varnish and wax? The fact that these materials never cross-link does not help in this case. They could never be removed from the painting just as if a completely insoluble varnish and adhesive had been used. What good is it that the new canvas backing can easily be removed from the reverse side if the painting itself stays soaked in wax and its color values are irreversibly changed?

Thoughts such as these are nothing new. Wolters, Messens and later Lodewijks, Makes, Hallström, Prescott, Berger and Zeliger have

previously noticed the changes caused by wax impregnation. The findings were brought to the attention of the conservation profession in demonstrations and publications (1,2,3,4,5,6). However, most owners are only too happy to get their paintings back in one piece again and looking "like new." Few are able to detect that the wax-lined painting looked like new because it was no longer the old painting. All its color values were insidiously changed. Such an overall change is understandably hard to detect and still harder to prove. If a color photograph was made before treatment which would show the difference, it could easily be argued that color reproduction is unquestionably unreliable. In fact, it is even hard to get two individual color photographs of the same subject to look identical. And what record could be made of the different textural values and nuances in gloss? These are gone forever. Thus, insidious damage has been done to the original painting since it has been irreversibly changed and the record of this change destroyed.

Looking at an old, cracked and torn painting we take into account that its appearance has changed. In the case of a painting which has been soaked in wax and varnish we are misled in believing that the painting is in perfect condition while in reality the conservator who performed the wax lining did not conserve the original at all.

Admittedly this is an extreme case. However, are not most modern paintings of the past fifty years painted in a similar way? Do not most modern artists utilize the play of light alternately reflected, from mat and glossy surfaces as well as from other textural differences to achieve part of their effect?

Could any wax-impregnated painting ever be brought back to its original form? No one will ever really know because the record has been irretrievably lost and there is no possibility of comparison. If complete removal of the wax were possible, theoretically it should bring the painting back to its original form. Unfortunately, there is growing evidence that this is impossible.

II. Irreversible Changes in Paint Films Due to Wax Impregnation

Restorers cleaning altar paintings have often noticed a marked difference between the parts contaminated by candle drippings and the rest of the painting. The contaminated areas were cracked and softened to such an extent that they could no longer be cleaned without loss of paint.

Doerner observes that paintings are easier to clean after they have been ironed with wax (7). His observation can only be true if varnish resins are softened by wax impregnation. Indeed, the mere fact that mixtures of wax, varnish resins and linseed oil are compatible indicates a mutual solubility of these materials.

Makes & Hallström were able to support the above observations with



Fig. 2

Artificially induced cracking through impregnation with mixtures containing beeswax (codes No.2 and 3), aged in the dark for 14 months at 54°C ($\pm 20^\circ\text{C}$). Note the sharp demarkation line between # 3 and # 4 (# 4 - microcrystalline wax).

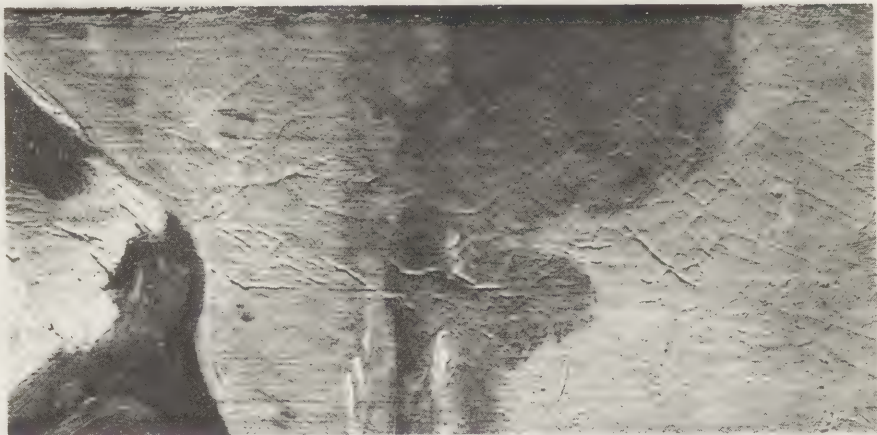


Fig. 3

Cracks of a type similar to the above have formed on a landscape by the American artist, Mortimer F. Lamb (born 1861). The painting was wax-lined in 1971.

chromatographic analysis (4). They impregnated specimens of a paint film from a 17th Century painting with wax, leaving adjacent parts of the specimens unimpregnated. They then extracted both the impregnated and unimpregnated films with alcohol and aliphatic petroleum fractions. Chromatographic analysis of the extracts showed that while both solvents had no leaching effect on the unimpregnated film, they had leached oleic and linoleic acid from the wax-impregnated paint film. In other words: Wax impregnation increased the solubility of the tested oil paint film to such a degree that even the most harmless solvents could not remove it without causing damage.

The Makes & Hallström tests provided additional proof to still more direct findings by Berger (8). In these tests specimens of oil paint films, 20cm x 4cm, were drawn from eight discarded paintings from the 16th Century through the 20th (1930). One-cm-wide stripes were marked on each specimen. Every second stripe was coated with one of the various resins either used or suggested for use in lining of paintings. Each coated stripe was separated from the next by one uncoated strip to serve as an untreated control. The specimens underwent a simulated lining on the vacuum hot table to assure even impregnation. They were then aged in the oven for six and twelve months at 54°C and 45% R.H. After aging the specimens underwent an abrasion test. An abrasion tester especially built for this test equally abraded the coated and uncoated areas. The test provided direct, visible documentation that the wax-impregnated stripes were more susceptible to abrasion than the adjacent uncoated ones and also some stripes coated with resins other than wax.

There was however an even more striking result: Impregnation with beeswax and wax-resin mixtures containing beeswax seemed to cause swelling in some of the impregnated paint films. This swelling in turn resulted in cracks of a typical configuration which we have since found on many wax-lined paintings (Fig.2,3).

The above tests may not be sufficient to declare that wax impregnation must harm all oil paint films. However, no one can foretell which oil paint film might be adversely affected by wax. Since most paintings contain a large variety of paint films, wholesale impregnation with wax is likely to affect some of them and, therefore, ought to be considered an indefensible gamble with the future of the painting even if no immediate results can be detected. In view of the tendency of wax to spread it is difficult to confine it to the area to which it is applied. Attempts to remove wax usually cause it to spread further. This makes even limited application of wax hazardous.

III Effects of Impregnation on Cellulose

Two adverse effects of wax impregnation have been discussed so far: First the staining of absorbent materials and, second, the swelling, cracking and softening of oil paint films. Since many paintings in the last century were painted on unprimed canvas, paper and cardboard,

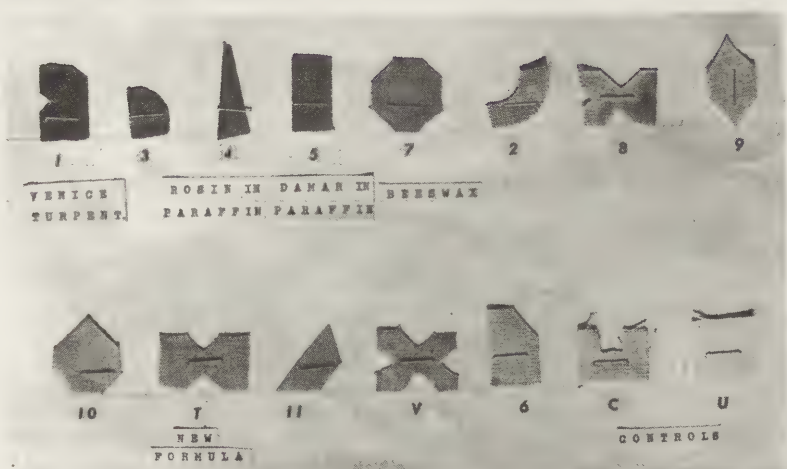


Fig. 4

Staining of canvas impregnated with adhesives and aged for five days at 95°C and 45% Relative Humidity. (See Table I).

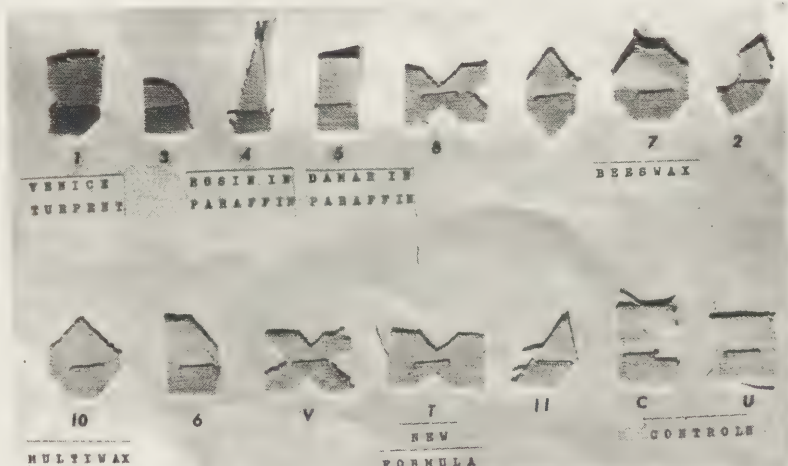


Fig. 5

Irreversible staining. Specimens treated as above, after prolonged extraction of resins with appropriate solvents still show considerable staining.

For explanation of code numbers please turn to the last page of this report.

Table I

Numerical Values for Interaction of Resins with Cellulose
(After aging at 95°C for three days)

Resin	Copper Number	Density	Folding MD	Folding CD
Unimpregnated, Unaged Cellulose	0.107	1.222	205 - 385	142 - 202
Aged Control	0.237	1.193	69 - 131	73 - 127
Microcrystalline Wax	0.230	1.200	<u>302 - 445</u>	191 - 281
Beeswax	0.477	1.184	162 - 268	49 - 169
Beeswax : Rosin (3:2)	0.358	<u>1.173</u>	<u>37 - 59</u>	<u>35 - 67</u>
Elvax ^R 40 in Paraffin	0.242	1.221	93 - 195	64 - 128
Venice Turpentine	No Data	1.164	31 - 65	<u>22 - 42</u>

Folding MD - Machine Direction, Folding CD - Cross Machine Direction,
Warp Weft

The above values were determined after extraction for three days in petroleum solvents, six days on a Soxhlet Extractor using methylene chloride followed by another three days in special solvents including ether and chloroform.

Folding strength = Mean of 21 determinations at 95% confidence level, (June 1968).

this research has also investigated the effects of impregnating resins on cellulose. Results of the investigation by Berger and Zeliger were first reported to the Third Plenary Meeting of ICOM in Madrid in 1972 (6). Their tests showed that impregnation with certain resins considerably strengthened decaying and brittle fibrous materials (These findings though fundamentally important for the preservation of all fibrous tissues, including canvas, are subject of another report).

In the course of the investigation it became evident that some waxes and resins interacted with cellulose. Acidic resins such as beeswax, rosin, Venetian turpentine and gum elemi caused considerable deterioration and staining of cellulose in accelerated aging tests of only three and five days' duration at 95°C (Table I and Fig.4,5). Moreover, some resins which were neutral at application such as rosin esters and polyterpenes, caused deterioration in these tests, probably due to the effect of their decay products.

In the same tests new cellulose tissues were strengthened when impregnated with microcrystalline wax and artificially aged, as shown by folding endurance tests evaluations. This strengthening effect persisted even after prolonged extraction of the microcrystalline wax (Table I). The latter suggested that microcrystalline wax was not completely removable from cellulose.

This hypothesis was tested by Zeliger in the following test (9): Samples of cellulose were impregnated with molten microcrystalline wax (Multiwax W. 835, Vitco Chemicals), aged for three days at 95°C, then subjected to solvent extraction. Specimens were extracted with a mixture of Benzene, acetone and methanol, followed by methylene chloride (Solvents strong enough to destroy any painting in seconds) until the extract showed no more ultraviolet absorption characteristic of the wax. Unable to remove all the wax it was decided to remove the cellulose. Specimens were then completely dissolved in nitric acid and fine fibers were observed floating up, unlike the unimpregnated control which stayed on the bottom of the beaker until completely dissolved. The acid solution was extracted with methylene chloride and the remaining extract showed ultraviolet absorption characteristic of the microcrystalline wax used for impregnation. The hypothesis that the impregnating wax could not be completely removed from the cellulose fiber was thus proven to be correct by two different tests: the folding endurance test and the chemical test.

Combined with the findings on the adverse effects of wax impregnation on paint films, this conclusion would be tantamount to a total condemnation of wax as a consolidant for paintings on canvas. In view of the serious implications of these findings it was decided to have the test repeated by another, independent laboratory. The test was repeated by Dr. David C. Locke, Professor of Chemistry, Queens College, New York, with identical results: Wax impregnation of cellulose fibers such as filter paper or linen yarn, cannot be totally removed by solvents. Wax impregnated cellulose samples were similarly tested: a. By extraction with heated solvents, and b. Without exposure to accelerated aging. In all these tests some wax remained in the cellulose though to a lesser degree than after accelerated aging.

IV Removal of Wax Coatings From Any Materials - Difficult

Removal of wax contamination is of considerable importance in adhesive technology. Few adhesives adhere well to wax, and the ones which do cannot form a strong bond because the wax being a soft material ruptures at low stress (Fig.5). Thus a wax coating interposes itself between the surfaces to be bonded and prevents any stronger adhesive from developing a firm bond (10). This quality of waxes is utilized in molding and casting. A wax coating inside a mold prevents the object being molded from sticking to the mold. Usually some of the wax coating sticks to the freshly molded object. This wax contamination must be removed before any additional parts, paint, etc. can adhere to the new object.

Table II

Effects of Solvents on Contaminants* Relative Ease of Removal of Contaminants by Solvent Series

Contaminants	Weak hydrogen bonding class			Moderate hydrogen bonding class			Strong hydrogen bonding class	
	2-ethyl- hexyl chloride	Methyl chloro- form	Tol- uene	Vinyl Tri- chloro- ethylene	2-ethyl- hexyl acetate	n-bu- tyl acetate	Cello- solve acetate	Cyclo- hexa- none Isopropyl alcohol
Abietic acid	C	C	C	A	B	B	B	B
Stearic acid	C	A	A	A	C	B	B	C
Photo resist	C	C	C	C	C	A	B	A
Fingerprint	B	A	B	A	B	A	B	A
Hand lotion	B	A	B	A	A	A	C	C
Detergent	C	C	C	C	B	C	C	A
Mold release (wax)	C	C	C	C	C	C	C	C
Grease	B	C	C	C	B	C	C	C
Silicone grease	C	C	C	C	C	C	C	C

* Levels of contaminant solubility based on Meseran values after solvent rinsing : A= contaminant effectively removed (16 or less Meseran units), B= partly soluble; longer rinse times should improve contaminant removal (17 to 99 Meseran units), and C= limited contaminant solubility in solvent (above 100 Meseran units).

Reprinted from Adhesives Age, December 1974, p.27.

Meseran units are determined by measuring the rate of evaporation of a carbon-14 tagged radioactive solvent from a surface by a Geiger counter. The degree of retention is a measure of contamination. The Meseran surface analyzer (ERA Systems, Inc., Chattanooga, Tennessee) was used in this investigation.



Fig.6

If a surface is coated with wax any added adhesive can only attach itself to the wax coating. Thus a chain is formed in which the wax is the weakest link. The chain breaks whenever the stress exceeds the adhesive strength of wax.

Following is a quote from a recent article in "Adhesives Age" which concerns itself with the problem of contaminant removal (11): "It (the wax, G.B.) must be a good mold release since none of the solvents had much effect on the removal of this contaminant. A couple of solvents might be used but a mechanical aid such as, scrubbing, may be necessary to help this contaminant removal" (Table II).

Naturally, it would be difficult to do any effective scrubbing within an impregnated paint film or canvas. Modern conservation practice rightly frowns upon scrubbing of paint films from the outside. Scrubbing could be especially disastrous if the wax has had a softening effect on the paint film, or when the paint film has the silk-like texture of many modern paintings so easily marred by scuffmarks (Fig.1). This would make wax impossible to remove without damage to the painting even if there were no direct chemical interaction between the components of the painting and the wax impregnation/coating. Wax impregnation of any and all the components of easel paintings must therefore be considered irreversible.

V. Changes in the Structural Integrity of Canvas Paintings

due to Impregnation

In the past thirty years or so wax impregnation has enjoyed considerable popularity as a consolidant for paintings because of the potentially damaging effects of animal glues which were used before. Exposure of canvas paintings to excessive humidity during application of the aqueous adhesives often led to immediate irreversible shrinkage of the canvas and resulting paint loss. Further damage was often due to shrinkage of the drying glue which sometimes caused distortions and cracking of the treated parts of the painting. These damages

grew with time because of the continuous movements of the aqueous glue during changes of relative humidity and temperature. In addition the bond between aqueous glues and oil paint is rather poor. The hygroscopic movements of the glue and the resultant distortion combined with its bad adhesion to oily materials often caused rapid bond failure, and thus failure of the consolidations done with glue. The complete removal of glue was only possible with water. Since most paintings contain glue as one of their structural components complete removal of the glue could not be accomplished without losses and dangerous weakening of the painting. The hardness of animal glue made its removal by mechanical means difficult and hazardous.

Compared to the defects of aqueous glues the structural weakness of wax seemed to be a virtue. Wax impregnation filled all the voids within a painting with wax thereby causing all the loose and brittle particles to again adhere to the canvas. This was accomplished without generating serious tensions because of the limited shrinkage of wax on solidification and also because wax, having no hygroscopic movements of its own, tends to reduce such movements in the impregnated painting. However, it was soon noticed that the structural strength of wax was insufficient to counteract serious stresses within the painting (12). Delaminations and cupping kept returning over and over again requiring repeated treatment.

The insufficient strength of wax, particularly microcrystalline wax, can be demonstrated by a simple experiment. A piece of microcrystalline wax may be pressed against a chip of heavily cupped paint of the kind found in the white impasto strokes of modern paintings. The wax will deform and make a mold of the cupped paint film with little or no effect on the paint film itself. The laws of action and reaction provide direct proof to the statement that the structural strength of wax is in no way sufficient to counteract the tensions which caused delamination of the much harder paint film.

The structural strength of waxes was tested by the University of Michigan. Following is a quote from its report: "The values for paraffin wax A at 35°C and beeswax B and casting wax G at 37°C were not reported, since these waxes were so soft they could not be measured reliably" (13). The values for proportional limits of elasticity of waxes are given in Table III, with the values for Beva added for comparison.

T a b l e III

Proportional Limit of Waxes at Various Temperatures (Lb/Inch²) *

Wax		23°C	30°C	35°C	37°C	40°C
Paraffin	(A)	262 (27)	53 (10)	-	-	-
Beeswax	(B)	80 (6)	60 (9)	28 (3)	-	-
Casting wax	(G)	148 (11)	56 (5)	22 (3)	-	-
Beva 371		500 (55)	350 (38)	No data	No data	148 (29)

* The numbers in parentheses are standard deviations (13).

There can be little doubt that the forces which cause a paint film or ground to tear loose from its support (to delaminate) are considerably stronger than can be developed by microcrystalline wax and even by any wax-resin mixture.

Another serious problem is the deformation of lining laminates caused by tears. The disruption of tension at the tear results in stress concentrations along the line of the tear which in turn cause distortions in the plane of the painting. Messens (14) and Berger (15) have tried independently of each other to solve this problem by connecting the edges of the tear with epoxy. Others have used different, less suitable, adhesives for the same purpose. In a wax-impregnated painting, however, effective bridging (joining) of tears is impossible, since no adhesive can develop a bond exceeding the structural strength of the wax coating to which it adheres. Thus once impregnated with wax, a painting is forever limited to the structural strength of wax. As the structural strength of its support decays the wax alone must provide more and more structural reinforcement in all tears and faults. The final result is a cracked paint film held only by wax and a brittle support which has only the structural strength of wax to depend on.

The structural weakness of wax has prompted wax liners to turn to solid supports (16). However, this approach can hardly be expected to solve the problem. Not only does a solid support completely obliterate the type of historical document lined on it and not only does it add considerably to the weight of the paintings, it also fails to achieve its purpose simply because the solid support does not change the basic equation of stress deforming the paint film versus structural or adhesive strength of wax. The solid support might be capable of eliminating the tensions caused by the stretching of the canvas. It might even hold the painting flat for some time because delamination at these small stress differentials is rather slow. However, if the stress which has originally caused the delamination of the paint film exceeds the adhesive strength of wax, delamination recurs. When recurring delamination of a wax-consolidated film shows the inadequate strength of the adhesive it is usually too late to do anything about it. The irreversibility of wax impregnation makes removal of the wax impossible, and no adhesive, no matter how strong, can ever form a bond on the structurally weak wax coating. A vicious circle of consolidation and delamination begins much to the detriment of the painting.

On solid supports such delaminations in wax-consolidated paintings is even harder to treat because the impervious backing permits treatment only from the face of the painting. Softening of the paint film with solvents or solvent vapors is only possible through the front. Removal of the painting from its solid support becomes extremely hazardous because the brittle paint film is in many places held only by the wax which is softened by heat when removal is attempted. Removal of a solid support by mechanical means is very expensive, especially from large paintings.

The recurrence of delaminations is quite frequent with heavily painted modern paintings where the stresses which cause cupping and delaminations are likely to develop even after lining. I have recently been confronted with a large painting by Kline, some 150cm x 200cm, which was mounted with wax on a Masonite panel because of cupping and delamination of the heavy paint film. When the condition recurred, repeated treatment became extremely expensive, and the owner decided to sell the painting immediately after 'consolidation' in order to get rid of the problem.

While the controversy of strong versus weak adhesives is by no means over, the irreversibility of wax coating prejudices all wax impregnated paintings for ever to treatments with weak adhesives.

VI. Undesirable Increase in Weight Due to Impregnation

In large paintings the weight is often to be blamed for distortions. Distortions are caused by viscoelastic movement of the laminate under the influence of gravity (creep). Tassinari has found that canvas is affected by creep even under minimal load conditions (17). The weight of a wax lining, combined with the plasticity of wax, increases the creep of the laminate under gravity and tension. Tassinari's and Mehra's investigations show that wax linings have three times the weight of glue linings of comparable resistance to creep (17,18). They have more than ten times the weight of Beva-Mylar or Beva-Fiberglass linings of comparable resistance to creep and to other damages. Resistance to creep is extremely important in large, modern paintings with heavy paint films which have a natural tendency to deform. In addition, the enormous quantity of wax and combustible cellulose used in the lining of large paintings can transform such paintings into gigantic torches in case of accidental fire.

VII. Destruction, Defacement and Obscuring of the Reverse Side of Paintings

In his previous report to ICOM the author called on fellow conservators to develop means which would protect the original support of the painting from decay. While in the past the reverse of a painting was generally disregarded, modern conservation practice aims at the total preservation of the historical document which naturally includes the support. Obscuring and staining of the reverse of a painting (canvas) by lining is not strictly preservation of the historic document, especially if such a canvas carries inscriptions or sketches. Makes, Hallstrom and Berger propose to use methods borrowed from textile and paper conservation to achieve total preservation. This is very necessary as the unprimed supporting canvas, cardboard or paper is often left uncovered and used as part of the artistic expression. Deacidification and treatment to prevent dirt absorption as well as structural reinforcement of the fibers might be

necessary to prolong the life of the supporting material. All these treatments are rendered impossible or ineffective by the irreversibility of wax impregnation (19). Materials are now available which permit the complete preservation of a painting both from its face and reverse. These materials permit reinforcement of the support without impregnation and without obscuring its reverse.

VIII. Summary

Research has shown wax impregnation of easel paintings to be irreversible. Irreversibility of wax is dangerous for the following reasons:

1. Wax stains many grounds as well as paint films and changes the appearance of texture.
2. Many waxes and wax-resin mixtures discolor in aging.
3. Wax swells many resinous and oil paint films and makes them susceptible to abrasion.
4. Beeswax causes cracking of some oil paint films.
5. Wax stains all cellulosic supports such as canvas, cardboard and paper. Some wax-resin mixtures might contribute to the decay of such supports.
6. Wax impregnation limits the structural strength of a painting and makes stronger consolidants ineffective.
7. Wax adhesives are heavy and suffer plastic deformation under weight and tension.
8. Wax lamination of large paintings constitutes a potential fire hazard.
9. Wax impregnation prevents the effectiveness of chemical treatments such as deacidification.
10. Wax impregnation prevents reinforcement of supports with modern materials such as polymer impregnation or the use of transparent films as lining supports.

New adhesives, better suited for conservation than wax-resin mixture have been developed. These adhesives underwent more severe tests than are usual in conservation of paintings. The Beva adhesives make lining of paintings without impregnation possible (20). They do not change the textural and other surface qualities of paintings. Beva adhesives permit the use of transparent and flexible secondary supports which enable the conservator to preserve unchanged all aspects of a painting, both from the front and the reverse.

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75/11/2-16

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Codes of the resins used to impregnate the canvas samples shown in Fig. 4 and 5

# 1	Venice turpentine	# 8	Damar in benzine
# 2	Rosin in benzine	# 9	Elemi
# 3	Canada balsam	#10	Multiwax
# 4	Rosin in paraffin	#11	Piccolastic A50 in paraffin
# 5	Damar in paraffin	# T	Thermogrip
# 6	Ketone N in benzine	# V	Victory White microcrystal wa
# 7	Beeswax		
# C Control, aged		# U Control, unaged	

The specimens in Fig. 5 were extracted in a Soxhlet Extractor for fourteen days with mineral spirits, trichloroethane, methylene chloride, alcohol and acetone. They were then immersed in chloroform and ether.

RELINING MATERIALS AND TECHNIQUES: SUMMARY OF REPLIES TO A QUESTIONNAIRE

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QUESTIONNAIRE ON LINING TECHNIQUES

The Madrid Conference of 1973 approved the circulation of the above questionnaire and this was carried out in due course through the kindly collaboration of the National Maritime Museum, Greenwich. Over 200 were sent out and 52 conservators replied.

The following summarizes the replies, mostly in the form of the numbers of conservators using the material, method, temperature etc. in question. It should be noted that the numbers do not necessarily add up to 52 since some questions were not answered, and some allowed the conservator to vote for more than one material or method. In some case the reply could be summed in a phrase which indicates sound conservation principles: "it depends on the particular painting".

Section A Lining materials

All conservators use linen; in addition 18 use fibre glass, 3 use terylene or other synthetic fabric, 2 cotton.
30 carry out marouflage on various secondary supports such as hardboard, perspex, fibre-board, aluminium sheet, paper, ply.

For interlining, 24 use paper, 15 felted synthetic fibre, 2 pelon, 1 silk chiffon,

To reduce weave interference, 11 avoid excess vacuum, 10 use cushioning on the table, 3 have painting face down, 3 fill weave interstices, 3 use closely woven linen, 1 matches the weaves of the two canvases.

39 select grade of canvas according to need, 12 use one kind only, 1 uses the smoothest possible.

The major problems encountered are : weave interference, sensitivity to relative humidity, relaxation, sagging, creep, the inelasticity (sic) of fibre-glass.

75/11/3-2

Section B Lining adhesives

The table shows the number of conservators who use the given adhesive regularly and those who have used it experimentally.

Adhesive	Regularly	Experimentally
animal glue base	6	13
starch base	2	15
wax/natural resin	39	47
wax/synthetic resin	5	10
synthetic resin (sol)	1	18
synthetic resin (emul.)	1	16
other various	1	7

In choosing the adhesive the following are some of the considerations: starch for 'modern' paintings, wax-resin if previously wax lined, the weight of wax-resin precludes its use for large paintings, optical objection to wax with certain types of ground.

The distribution of 'melting points' of wax-based adhesives used was as follows:

°C	Number of users
50	1
55	7
60	12
65	15
70	5
75	2

The replies to the question about the ageing of adhesives reflect the wax versus glue controversy:

"wax-resin produced degradation of the canvas fibres"

"wax-resin of 1930 showed embrittlement"

"100 year old wax lining satisfactory"

"depends on the climate, 200 year old linings perfect"

Several conservators report increased brittleness of wax/resin.

"sturgeon glue is the finest of fish glues"

"paste and wax/AW2 linings delaminate after a few years"

All in all the replies are too divergent for conclusions to be drawn on the relative merits of the wide range of adhesives mentioned.

Section C Impregnation Techniques (applicable to wax/resin users only)

The answer to the question: do you impregnate before lining? was as follows.

	Yes	No	Depends on case
(a) picture canvas	37	2	7
(b) lining canvas	32	10	3
Do you remove dressing prior to impregnation?	30	15	2

18 conservators wash the canvas in the stretched condition, 18 wash it before stretching. 14 stretch the canvas in the wet state and 28 dry it before stretching.

33 answered No, 5 Yes, and 6 that it depends on the case to the question: do you stretch the painting prior to impregnation?

11 said they face the painting before impregnation, while

12 said it depended on the case.

The choice of medium for facing was as follows:

14 wax based, 7 starch, 5 synthetic resin, 3 animal glue.

Most preferred to remove old lining adhesives dry by mechanical means.

The main problems encountered in the impregnation were: gauging the quantity of wax, securing even distribution, distortion and shrinkage, the additional weight.

Section D The lining process.

Part 1, wax/resin.

Vacuum hot-tables are used by 80% of the conservators replying. All are aluminium topped except for 3 stainless steel, 1 glass, 1 anodised aluminium. All are electrically heated except 2 which have hot water. 15 use electrically heated rubber pads. The mean heating time is 20 minutes but the range is from 5 minutes to 1 hour. For most the cooling time is from 15 to 30 minutes; 40% of the tables have cooling fans, 2 have lift off tops, and water can switch to cold.

The temperature reached by the table surface ranges from 50 to 80°C but most operate in the 65° to 70° range. The painting temperatures are given as 5° lower, the surface of the diaphragm exposed to the air being a further 5° lower.

The degree of vacuum employed ranges from 100mm to 700mm the most common being 500mm (approx $\frac{2}{3}$ atmosphere)

To the question: do you line with the facing on? 11 said yes, 15 no, 13 depends on the case. 26 sometimes resort to having the painting face down on the table.

15 never hand line, 12 do occasionally, 19 do so regularly.

Irons range in weight from 0.5 to 5 kg operating at 65°C.

In hand lining 20 conservators have the lining canvas stretched and 9 do not. Similarly 6 stretch the painting and 23 do not.

The major problems encountered in the wax/resin process (hand and vacuum table) were: weave interference, air pockets, trapped solvent, optical changes, the effect of heat on modern paintings.

4 conservators replied yes, 8 no, and 26 depends on the case, to the question: do you wax/resin impregnate without lining?

75/11/3-4

Section D The lining process.

Part 2 Adhesives other than wax/resin.

The use of adhesives other than wax has the following distribution:

13 use animal glue and/or starch compositions to various formulae, 12 use polyvinyl acetate, 8 BEVA.

7 conservators do not apply heat in the process, others operate at about 60°C.

15 reported using vacuum pressure.

Mechanical methods of removing old adhesive are preferred.

Most iron with the painting face up; up or down, heavy impasto is protected by cushioning.

On the question of stretching the painting prior and during the process the answers were:

	Yes	No	Depends on the case
prior	9	15	5
during	4	22	2

The lining canvas is stretched by 18 conservators, not stretched by 10.

9 say they have the facing on, 8 off during lining; 8 say it depends.

Most conservators treat flaking before the actual lining: 25 answered yes, 2 no and 1 occasionally. Only two impregnate without proceeding to line; 13 do not and 4 may occasionally.

In addition to the foregoing replies, many conservators submitted particular comments but these were too varied, numerous and often conflicting for definite conclusions to be drawn. They serve to show that there is nothing static about the art of lining, whether in terms of the materials or the procedures. It seems likely that the general outlook will have changed somewhat since the survey was made, particularly through the stimulus of the 1974 National Maritime Museum Conference on Lining.

SOME EMPIRICAL DETERMINATIONS OF THE STRAIN DISTRIBUTION IN STRETCHED CANVASES

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Abstract

The strain distribution in raw stretched canvas, impregnated lining canvas and a painting stretched by the 'Dutch method' was measured using a grid system. The purpose was to provide some basic empirical data with which to describe the various situations, and to serve as a reference point in the construction of a mathematical model.

The most significant results were the heterogeneous nature of the strain distribution, the role of the Poisson effect in the distribution, the influence of the anisotropy of canvas and the occurrence of the largest strains at the corners of stretched canvases.

Introduction

The stretching of canvas paintings is a process which subjects all the component layers of a painting to various stresses and strains. Any painting will encounter this application of stress many times in its existence, most notably when the stretcher keys are tapped out, but also after a lining operation when the lined painting must be completely restretched.

This stretching process undoubtedly exerts its influence on the manner that a painting deteriorates. The most obvious example of this is the way that 'mechanical' cracking develops in the paint and ground layers. It is only necessary to compare the completely different types of cracking which occur on panel paintings with that on canvas paintings to illustrate this point. There is often a tendency to ascribe the forms of 'mechanical' cracking in canvas paintings solely to the different climatic conditions between areas backed by the stretcher and those open to the environment. But this phenomenon cannot account for such types of 'mechanical' cracking as the cracks at the corners of paintings which run at 45° to the axes of the painting or for spiral cracks which are so frequently seen. The reality is that all 'mechanical' cracks develop under a complex interaction of stresses and strains from a variety of sources, a major component of which is provided by the stretching of the painting.

painting.

However, our knowledge of exactly what distribution of stresses and strains is imposed on a painting by stretching is extremely limited. Unfortunately, mathematical determination of this, even in a stretched canvas alone is a complicated affair. This is because the way that artists (+ conservators) stretch canvases by applying point loads secured, usually with tacks, at a point gives rise to an extremely heterogeneous straining and also the strains are often very much larger than the 'small strains' which mathematical analysis is normally restricted to. Nonetheless steps are being taken by researchers to provide a mathematical solution.

The purpose of this paper, however, is to approach the problem not from a theoretical determination of stress/strain distribution but instead to take actual measurements from stretched samples and to arrive in that way at an empirical determination of the distribution.

Experiments were performed on stretched canvas in order to isolate the behaviour of that material under stretching, the work will hopefully be extended in the future to deal with canvases coated with ground and paint layers.

Experimental Procedure

Three series of experiments were conducted, to examine the stress/strain distribution in stretched raw canvas, in the same canvas impregnated with a wax/resin lining mixture and in a painting drummed by the 'Dutch method'. The details of the canvas are given in Appendix I.

The technique used to determine the strain distribution in all the experiments was a grid method. In this method a grid is drawn on the unstrained material and then photographed under standard conditions. The material is then stressed and re-photographed in this state. From the initial and final photographs the strain distribution may be determined from the grid deformations.

The grid system was chosen because it gives an overall indication of strain distribution and because it is relatively simple requiring no sophisticated equipment. It should, however, be noted that it does lack accuracy and cannot be used to detect very small strains. However for the purposes of this investigation it proved to be an adequate method.

1. Stress/Strain Distortion in stretched raw canvas

The first experiment was carried out on an unwashed piece of the raw canvas. A piece of the canvas approximately 60 x 40 cms. was lightly pinned on a drawing board so that it was flat, but not distorted or significantly stressed. A grid was then drawn on the canvas of lines 1 cm. apart running in the weft and warp directions. Several small circles were also drawn at points such as the centre of the grid and the perimeter of the canvas. The canvas and a scale

were then photographed under standard conditions.

It was then stretched, in the usual manner, on a stretcher 41 x 33 cms., the grid was not observed during stretching in order to avoid prejudicing the procedure. The canvas was however placed on the stretcher so that the warp and weft lines ran parallel to the edges of the stretcher. Hence the applied load during stretching was in the warp and weft directions as is normally the case in the stretching of canvas. The aim of the stretching procedure was to produce the sort of distortions commonly observed on old painting canvases.

The strained canvas was then photographed, with a scale, under the same conditions.

The two photographs were then printed on 38 x 30.5 cms. photographic paper and dry mounted on card. The measurements of strain were then taken from the two mounted photographs.

Results

From the photograph of the strained canvas several features were apparent. The general appearance of the deformed grid was similar to the distortions of weave that are frequently seen on canvas paintings. The grid was sharply distorted and except for a region in the middle was mostly heterogeneously deformed (i.e. lines which were straight and uniformly spaced did not remain so after stretching). This was particularly apparent at the edges where the grid lines were 'scalloped' towards the securing staples indicating areas of stress concentration.

All the circles had deformed to ellipses (or approximate ellipses). The major axes of these ellipses indicated the direction of maximum principal strain and the minor axes the direction of minimum principal strain.

Measurements of the strain were taken by measuring both the change in the grid and in the circles.

The circle deformations were recorded by drawing the original circles over the deformed circles on the photographs of the stressed canvas.

This indicates the major and minor axes of the ellipse (i.e. the deformed circle), the lengths of these can then be recorded and compared to the original circle diameter. In this way the maximum and minimum principal strains and their directions were determined. It is clear that in general when a circle has been deformed into an ellipse the major axis will correspond to an extension strain and the minor axis to a compression strain. The points of intersection of the circle and ellipse are the directions of zero strain.

This is illustrated in Fig. I below:

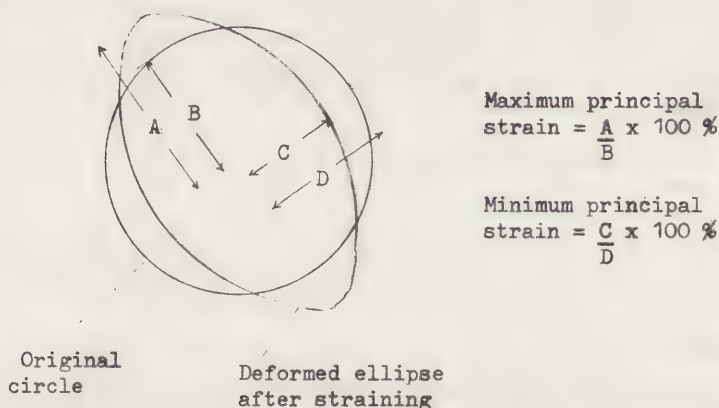


Fig. 1 Determination of maximum and minimum principal strains from a strained circle.

Fig. 2 shows a sketch of the stretched canvas on which the directions of the maximum principal strain e_1 (i.e. the largest extensional strain) and the minimum principal strain e_2 (i.e. the largest compressive strain) and their magnitudes, determined from the strained ellipses are shown. The principal strains are drawn to scale according to their magnitudes. An examination of Fig. 2 shows at once that the majority of the principal strains are inclined at an angle of approximately 45° to the warp and weft. At the centre of the canvas the value of e_1 is 5.5% and that of e_2 is -1.5%. However as the 4 corners are approached the values of e_1 and e_2 become considerably larger and tend towards values of e_1 around 13% and of e_2 around -8%. Thus it is clear that the corners of the stretched canvas are areas of stress concentration. Particularly noteworthy is the orientation of the strains at the corners; this is that the extensional strain runs at 45° clockwise to the warp direction and the compression strain at 45° counterclockwise to the warp direction. This at once brings to mind the mechanical cracks which often occur in the corners of canvas paintings at precisely the same angles. Although generalisations should be avoided it seems clear that this sort of strain distribution phenomenon probably contributes to the formation of such cracks.

It is also important to note the magnitude of the strains which are relatively large but clearly not uncommon in stretched canvases.

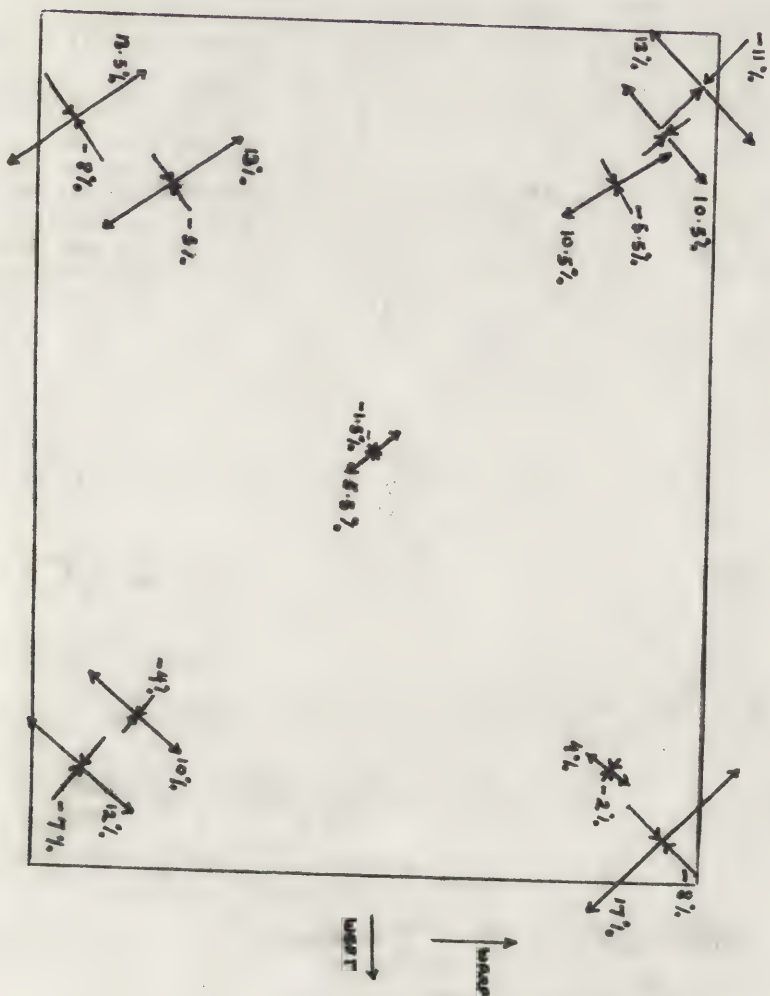


Fig. 2 A plan view of the stretched canvas showing the directions and magnitudes of the principal strains, as determined from the strained circles.

The measurements of strain using the grid lines as a reference were performed using Fischer's Method (see Appendix 2). This allows the strain along any one grid line to be determined, it is particularly useful in detecting stress concentrations. In the method measurements are taken along a particular grid line and a graph is produced whose x axis represents the distance along the grid line and whose slope at any part is equal to the strain at that point. Thus a positive slope corresponds to a tensile strain and a negative slope to a compressive strain. The method has two main advantages. Firstly, a point which deviates excessively from the curve may be immediately checked. Secondly, it provides a continuous curve representing the whole line at all points whereas the standard computational methods must select specific points.

The strains along 6 separate grid lines were calculated by this method. The lines chosen were the central grid lines in both the west and warp directions and 4 lines running parallel to the perimeter of the canvas and very close to the edge. The location of these 6 grid lines is shown in Fig. 3.

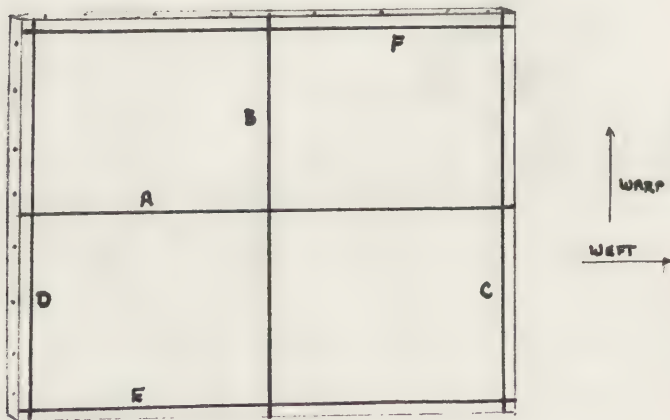


Fig. 3 The location on the stretched canvas of the six grid lines along which Fischer's method was applied.

Figs 4-9 show the curves that were obtained by applying Fischer's Method to these lines. It should be emphasised that the slope of the graphs indicates the strain in the direction in which the line runs. Thus for a line which runs in the weft direction, the strains computed are strains in the weft direction. The curves have been simplified so that the main trends in the strain distribution can be clearly seen. The measurements along the lines were taken with the left hand edge and the bottom edge of the stretcher as the zero reference points.

It is convenient to deal with these line in 3 sets of pairs. Figs. 4,5, show the curves obtained for the central lines in the weft and warp directions respectively. The slope of both these curves is always positive which indicates that they are under tensile strain. But the curves can both be divided into 3 sections, a middle zone of lower slope and two outer regions near the edges of the canvas of higher slope. What this means is that in the regions close to the edges of the canvas there is a greater tensile strain exerted on the canvas than in the centre of the material.

In the weft direction the mean values of the strains in these 3 zones is 2.25% at the left border, 1% in the centre, and 3% at the right border. In the warp direction the strains are appreciably larger and have values of 4.5% at the bottom border, 2.25% in the central area and 5.5% at the top border. This difference in strain magnitude between the warp and weft directions is of course to be expected since it is a well known property of canvas that a given load will produce greater extension in the warp than in the weft.

On both curves there are aberrations from a smooth curve. These are due to local stress concentrations but these aberrations which are much more noticeable in the weft direction (Fig 4) are not a major feature of the strain distribution.

The next pair of curves Figs. 6,7 represent the lines that run in the weft direction parallel to the top and bottom edges of the stretcher. The most striking feature of these two graphs is that they are both of negative slope. This means that in the weft direction the canvas has suffered a negative strain or in other words been compressed. The reason why this has happened is because the lines run very close to the edge of the stretcher where the force was applied in the warp direction. This has produced a Poissons ratio effect in the weft direction which has compressed the weft direction. The only force acting to counteract this compression is that applied in the weft direction at the points corresponding to the top and bottom grid lines. The effect of this force can be seen in that at the beginning and end of both slopes, i.e. the points nearest the applied force, the slope of the graphs is reduced. But this is only a localised edge effect which does not counteract the dominant effect of the load applied in the warp direction to contract the canvas in the weft direction.

A second feature of both these curves is their descending step like appearance. This is because there are many zones of high stress concentration, caused by the points at which the canvas is secured, which interact with the general strain distribution. There are even points of zero slope (indicating zero strain) which occur where the

pull in the warp direction was not directly applied.

Along the grid line at the bottom of the canvas (Fig. 6) the strain is on average -6% and along the line at the top (Fig. 7) it is -3.25%. In both graphs, in the regions where the stress was not directly applied zero strains are indicated by the zero slope of the graph. In addition at the corners where the Poissons ratio effect is counteracted by an applied pull in the weft direction reduced strains of between 0% and -1.5% were recorded. There are one or two areas of positive slope (or extensional strain) in both curves which generally occurred on the borders of areas where the warp load was applied.

The final pair of curves Figs. 8, 9 show the strain distribution in the warp direction along the left and right borders of the canvas. These curves again fall into three zones, a middle area of negative slope indicating compression and two outer areas of positive slope indicating extension. This means that near the top and bottom of the stretcher the canvas has been extended in the warp direction, whereas in the middle it has contracted along these grid lines. The explanation of this is straightforward, in the central region the Poisson ratio effect of the load applied in the weft direction on the right and left borders has produced a net contraction in the warp direction. However, towards the top and bottom edges this Poisson effect has been counteracted and overcome by the force applied in the warp direction parallel to these grid lines. This has produced a net extension in the warp direction.

The difference in the form of the graphs of Figs. 6,7 and Figs. 8,9 is explained by the anisotropic nature of canvas. The extension in the weft direction is less than in the warp direction for a given load because of the way that canvas is constructed. The effect of this was shown in Figs 4,5 where the weft extension was approximately half the warp extension. This has a corresponding influence on the Poissons ratio effect. A lower weft extension produces a still smaller warp contraction. Thus although the central zone of the grid lines shown in Figs. 8,9 was contracted, this contraction was easily overcome at the top and bottom because the load applied in the warp direction along these lines produced a relatively large strain in the warp direction. Hence the formation of the 3 clearly defined zones.

In the lines parallel to the top and bottom of the canvas (shown in Fig 6,7) exactly the opposite situation prevailed. The high strain in the warp direction produced a smaller but relatively large Poissons ratio effect negative strain in the weft direction. This was not significantly counteracted, except very near the corners, by the applied load in the weft direction because the weft direction extends much less for a given applied load. Returning to Fig 8,9 it was found that at the left hand border the values of the strains in the warp direction were +2.0% at the bottom of the canvas, -2.0% in the middle of the canvas, and + 2.0% at the top. On the right hand border the strains were +2.25% at the bottom zone, -1.5% in the middle and +2.0% at the top.

There are areas of stress concentration particularly right at the corners but in general the curves are smoother than these of Fig 6,7.

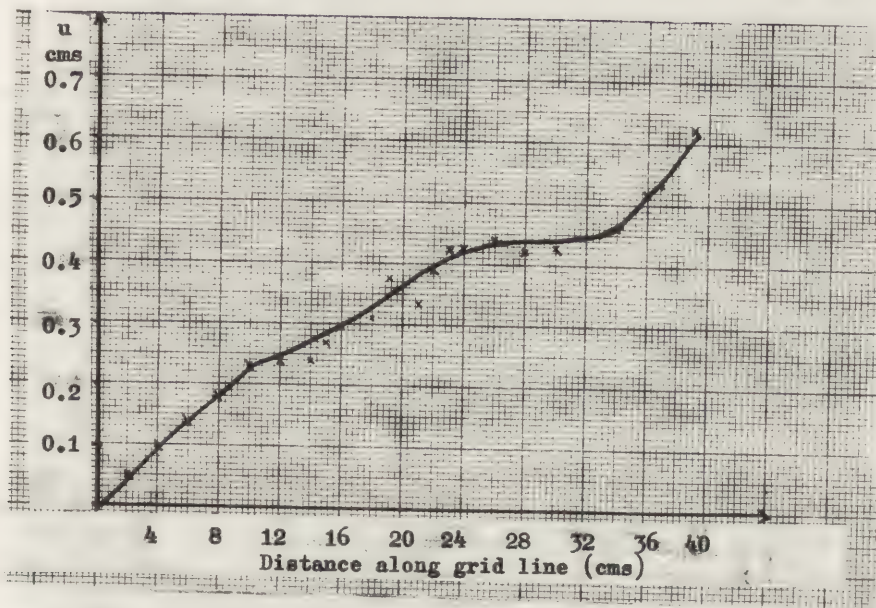


Fig. 4 Application of Fischer's method along the grid line A.

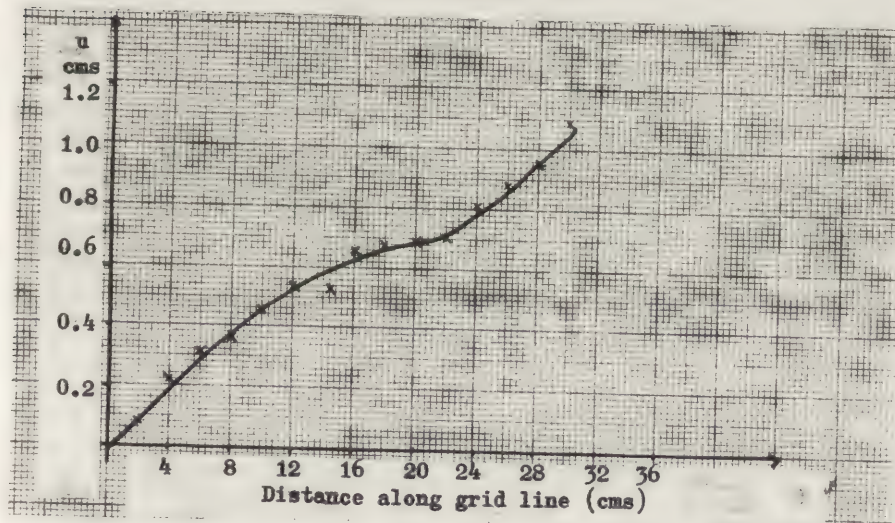


Fig. 5 Application of Fischer's method along the grid line B.

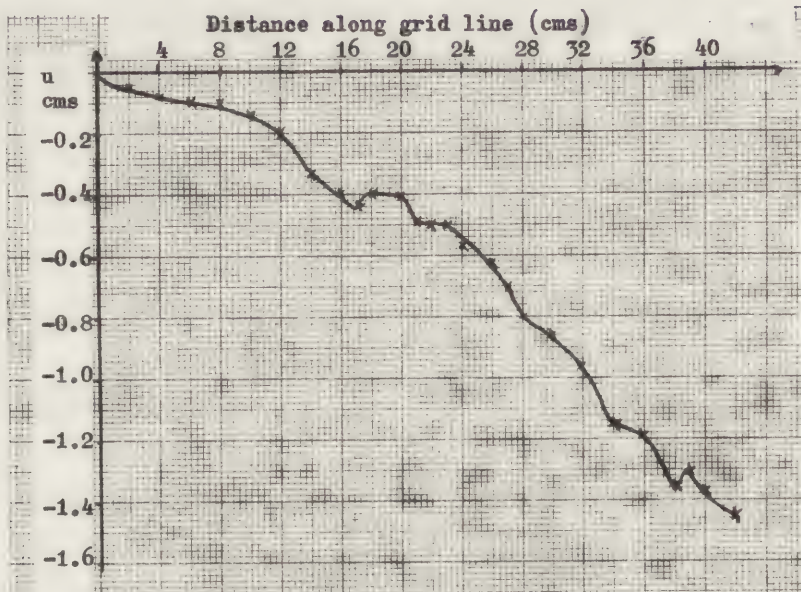


Fig. 6 Application of Fischer's method
along the grid line E.

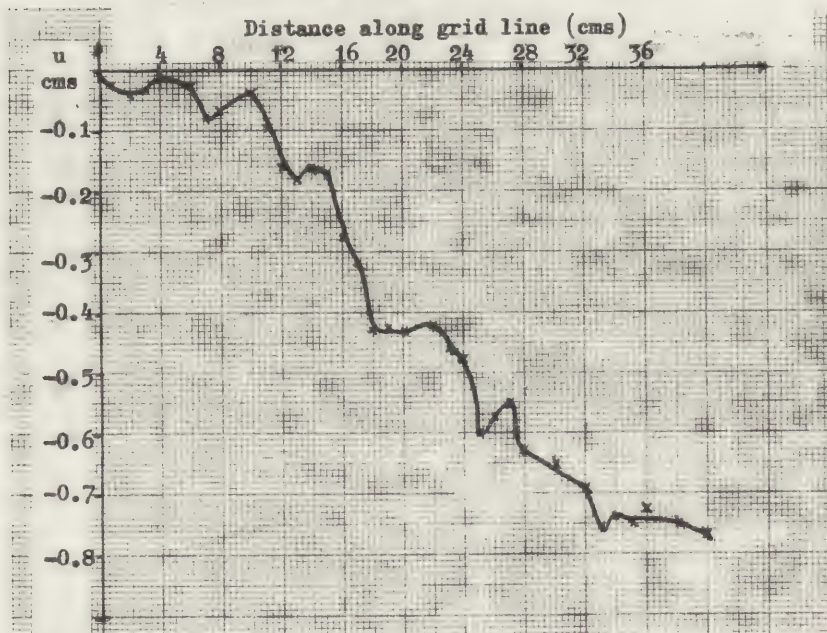


Fig 7 Application of Fischer's method
along the grid line F.

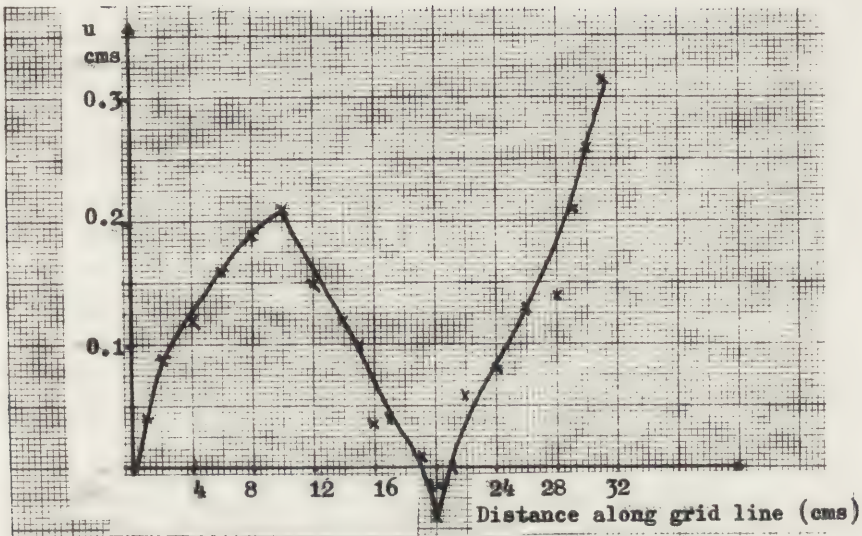


Fig. 8 Application of Fischer's method along the grid line D.

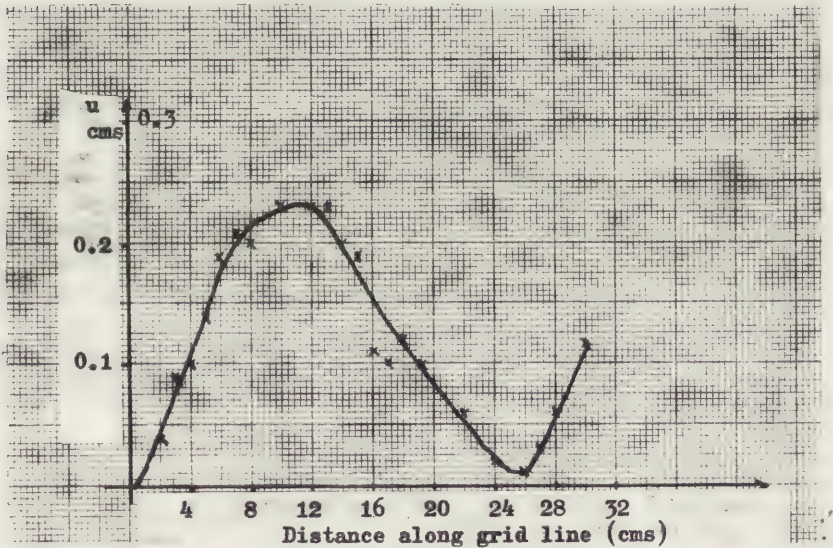


Fig. 9 Application of Fischer's method along the grid line C

This is again due to the greater resistance to straining of the weft direction of the canvas.

Conclusions

It must be borne in mind that only limited conclusions can be drawn from the results of this experiment which was performed with only one type of canvas on a particular type of stretcher, nonetheless the similarity of appearance of the weave distortion of stretched canvases implies that some general conclusions can be made. At least the following points can be concluded:

1. The stress/strain distribution in a stretched canvas is a very complex situation involving large areas of heterogeneous strain. It will clearly be a function not just of the properties of the material but also of the manner in which it is stretched and the dimensions of the stretcher as well as the alignment of the warp and weft.
2. In the stretching of new canvas large strains can easily be generated even of an order of magnitude of 10% - this presents considerable problems for mathematical analysis of stress/strain distribution.
3. Stretching a canvas does not imply that the whole canvas is extended, many directions on the canvas will in fact suffer compression as a result of the stretching process. This has important implications in the way that a stretched canvas may influence the layers which it supports, since cracking occurs by buckling of the paint as well as by tensile fracture.
4. In the experiment conducted the largest strains were found at the corners of the canvas at angles 45° to the weft and warp. It is unwise to generalise too much from this but experience does indicate that this sort of strain distribution is quite likely. The fact, for example, that lined paintings frequently shear at the corners is consistent with the corners being areas of high strain. In addition the frequent occurrence of cracks at 45° to the corners suggests that the direction of the principal strains may well generally be at this approximate angle. This is further implied by the fact that at an angle of 45° to the weft and warp, canvas frequently extends as much as 5 times more than it does in the warp direction for a given load, so maximum strains would naturally tend to occur at this angle.
5. The anisotropy of canvas has a pronounced effect on the stress/strain distribution in stretched canvas. This was most clearly indicated by the strains determined around the perimeters of the test piece. This makes ^{the} value of the Poissons ratio for any given direction of particular importance in determining whether positive or negative strains will be produced.

2. Strain Distribution in an impregnated canvas

The second series of experiments were aimed at measuring the strains in a canvas during its preparation for use as a lining material with beeswax/resin adhesive.

A piece of raw canvas was first stretched on a stretcher 60cms x 90cms and a grid of lines 2.5 cms apart was drawn on the stretched canvas together with a series of circles. This was photographed under standardised conditions. A wax/resin mixture (90% beeswax, 10%AW2) was impregnated into the canvas while it was on the stretcher. A new photograph was taken and this was compared with the initial photograph. No observable difference was found between the two photographs, it was therefore concluded that no measurable strain (i.e. less than 1.0%) had been imposed as a result of the impregnation.

The impregnated canvas was next removed from the stretcher and heated under vacuum on a hot table. After this 'lining' process it was rephotographed and measurements were taken by comparing the final and initial photographs.

From the fact that straight lines had remained straight and uniformly spaced, it was evident that no heterogeneous strains had resulted from the heating under vacuum. However it was found that the canvas had relaxed during the process. The lines through the centre of the canvas in the warp and weft directions had both decreased by about 2% and this was also reflected in a similar change in size of the circles.

The last stage was to re-stretch the impregnated canvas on the 60 x 90 cms stretcher and photograph the restretched canvas.

From a comparison of this photograph and the initial one, the following points could be made:

- (i) The area of heterogeneous deformation was much smaller than for stretched raw canvas. It extended for only the first 3 grid lines from the edges.
- (ii) The largest strains occurred at the corners with the principal strains at these points running at 45° to the warp and weft. Though in this case the positive and negative strains were in the opposite directions to those found on raw canvas. The principal positive strain was 6% and the minimum principal strain was 0% at the corners.

Conclusions

The effect of wax/resin impregnation on stretched canvas strain distribution can only be tentatively indicated from the experiments. It does seem likely though that two important factors come into operation.

1. The canvas has a tendency to relax during heating under vacuum pressure. This is presumably because the 'locking' effect of the wax/resin mixture ceases to function when the mixture melts.
2. Wax/resin impregnation modifies the mechanical properties of raw canvas by at least initially making the material more isotropic and by increasing the modulus of elasticity. This was indicated by the

more uniform strains in the warp and weft directions and by the fact that lower strains had to be imposed in order to obtain a taut canvas.

As a result of these conclusions experiments were performed to determine in more detail the effect of wax/resin impregnation on canvas properties, these are reported in a separate paper.

3. Strain Distribution in the canvas of a drummed painting

The 'Dutch method' of stretching a painting prior to lining it, is frequently used by restorers. The stresses and strains imposed by this technique are completely unknown and it was therefore decided to try and study them using the grid method.

An unimportant painting (60 cms x 50 cms) which was undistorted was used. On the reverse of the canvas a grid of lines 1 cm apart was drawn together with some circles. The grid was recorded photographically.

The painting was then 'drummed', using brown paper strips 15 cms wide, secured to the edges of the painting and to an auxiliary stretcher. The canvas was kept taut for two weeks during which time the paper was regularly subjected to cycles of wetting and drying. It was then rephotographed.

Results

It was found from comparison of the initial and final photographs that there was no visual difference at all. There was no apparent deformation of the grid lines after stretching. Measurements taken from the photographs also indicated no measurable difference between the stretched and unstretched state.

It is evident that the strains imposed were not measurable by the grid method, that is they were of an order of magnitude of less than 1%. This is in itself an important conclusion but a detailed investigation would require the use of more sensitive equipment such as strain gauges. Of course the low strains involved do not necessarily imply low applied stresses since we are dealing in this case not with a raw canvas but with a canvas, ground, paint composite which will have considerably different properties. These are however matters for further study.

General Conclusions

The purpose of these empirical investigations into stress/strain distribution in stretched canvases was to attempt to gain some initial information in what is at present a new field of study for conservators. The results of the experiments are not intended as definitive descriptions of each situation, rather they serve to indicate the sort of distributions that can occur and the order of magnitude of the changes involved. Taken in this light the experiments do at least give a qualitative indication of the nature of stress/strain distribution in various circumstances and of the interaction of materials and directional properties which cause it. They also help to indicate the

conditions which a suitable mathematical model must satisfy if it is to adequately describe stress/strain distribution in stretched canvas as it is actually encountered by conservators.

APPENDIX I

Canvas Details:

Material: Linen	Construction: Plain Weave
Warp: 31 ends/cm	Weft: 29 ends/cm
Yarn diameter: 0.15 mm	Weight: 0.014 gms/sq.cm
Mean thickness of canvas: 0.24mm	Suppliers: Roberson, Parkway, London N.W.1.

Suppliers description of canvas: O grade

APPENDIX II

Fischers Method

Suppose there are a number of points A_0, \dots, A_n on a straight line parallel to the X axis. Let X_0, X_1, \dots, X_n be the X co-ordinates of these points before the body undergoes deformation. After deformation suppose these points move to other new positions, A'_0, A'_1, \dots, A'_n and the X co-ordinates are X'_0, X'_1, \dots, X'_n . Now if we denote the displacements in the X direction by u these are $X'_0 - X_0, X'_1 - X_1, \dots, X'_n - X_n$ for the points A_0, A_1, \dots, A_n .

If the u values are plotted against the X co-ordinates of the undeformed positions a curve will be obtained whose slope at any point $\frac{du}{dx}$ corresponds to the strain in the X direction at that point.

This is illustrated by consideration of the figure below:

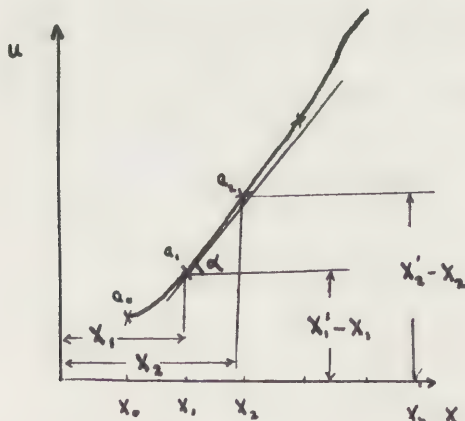


Illustration of Fischer's Method

75/11/4-16

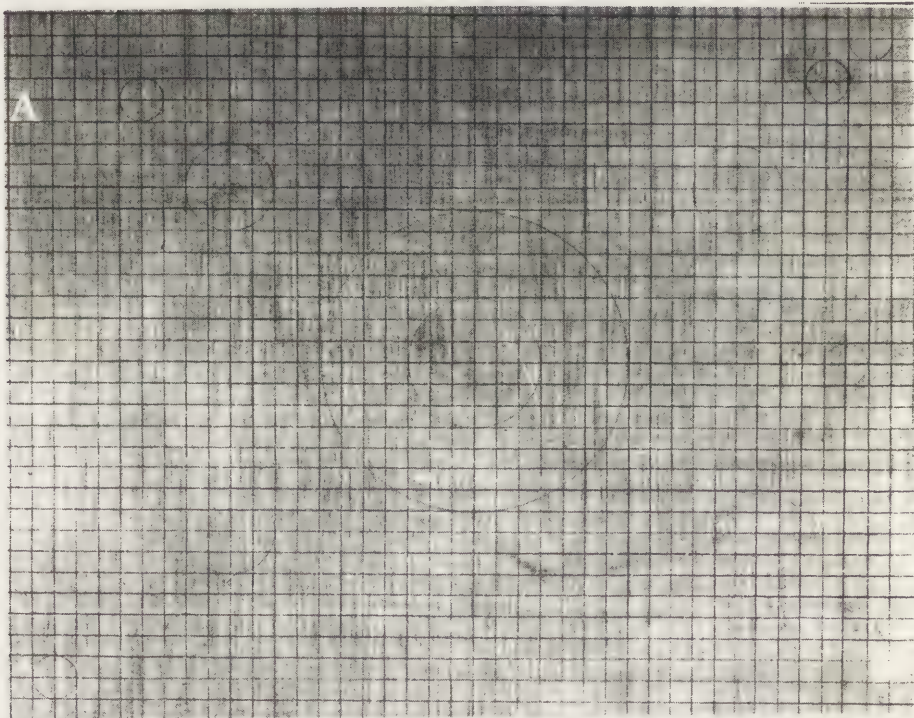
Consider point a, ,

$$\begin{aligned}\frac{du}{dx} &= \tan \alpha = \frac{(X'_2 - X_2) - (X'_1 - X_1)}{X_2 - X_1} \\ &= \frac{(X'_2 - X'_1) - (X_2 - X_1)}{X_2 - X_1} = \frac{\Delta l}{l} = \text{strain in X direction}\end{aligned}$$

Thus measurements need only be taken of the change in the X co-ordinate location of the points (i.e. the grid intersections) and then to plot these points against their original location in order to obtain a graph whose slope at any given point is the strain at that point. This was the method used in order to measure the strain along given grid lines.

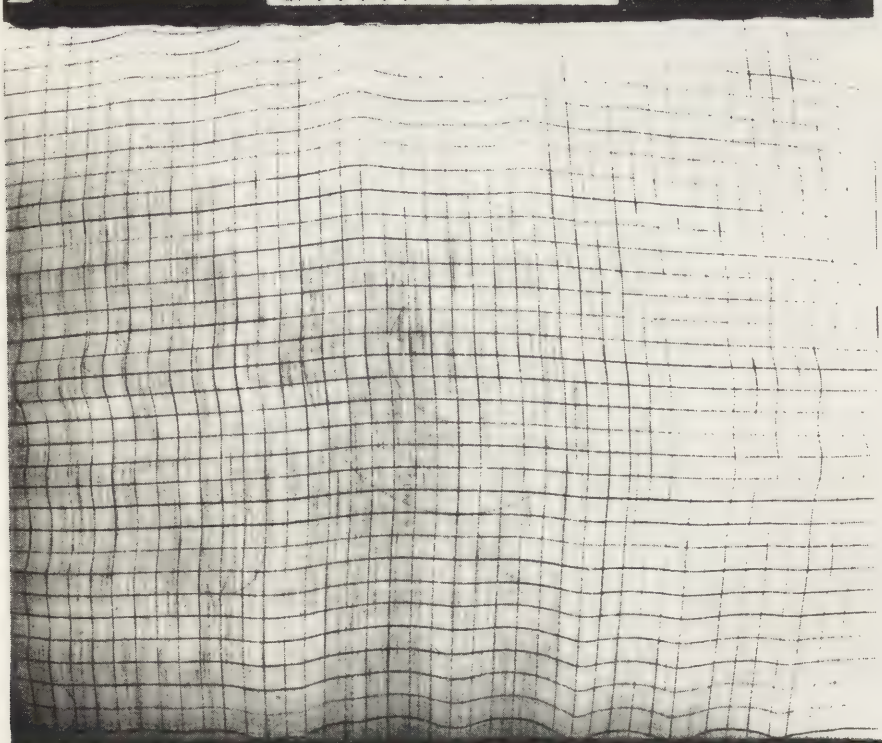
APPENDIX III

Photographs of raw canvas in experiment 1.



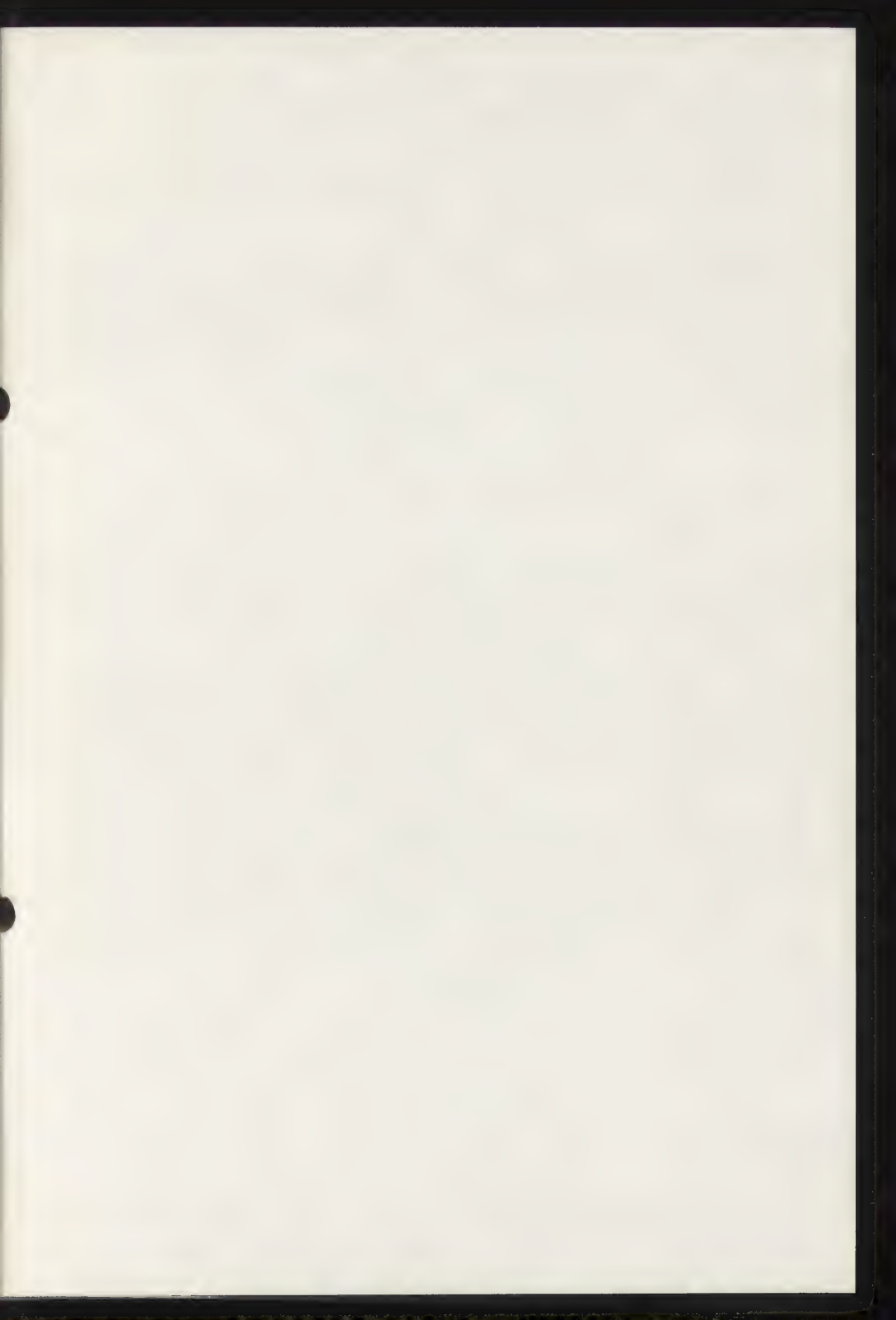
Photograph A: This shows the raw canvas in the un-stressed state with the grid lines and circles drawn onto it. It is important to note that the grid lines were drawn parallel to the warp and weft threads of the canvas.

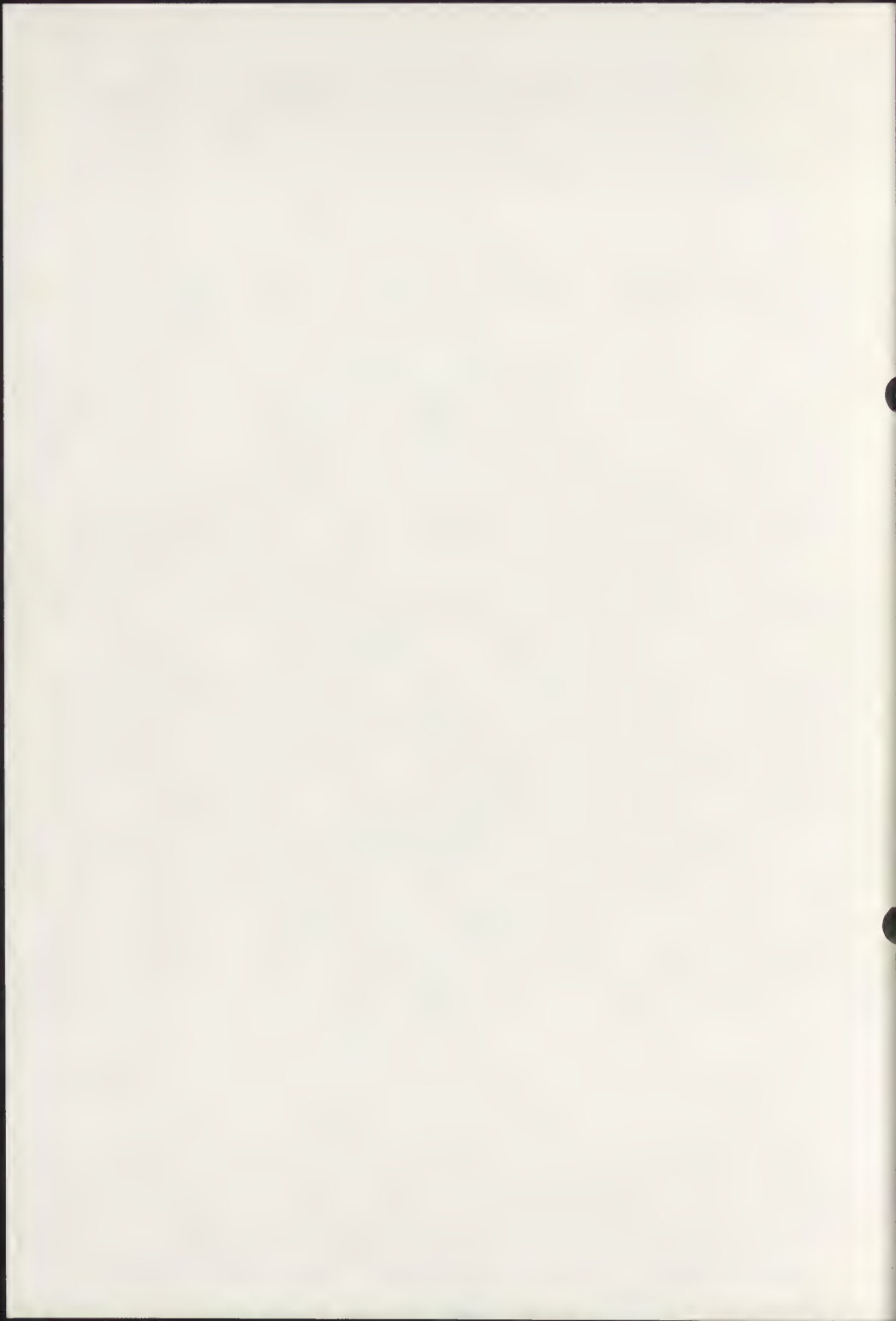
B



Photograph B This shows the same canvas after stretching over the stretcher. No attempt was made to keep the warp and weft threads parallel with the stretcher edges, the canvas was instead stretched to create the scallop type distortions frequently seen at the borders of stretched canvas.







FURTHER DEVELOPMENTS IN COLD-LINING (NAP-BOND SYSTEM)

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This contribution to the Working group on Stretchers and Lining of the ICOM-conference 1975 is a summary of studies undertaken at the Central Research Laboratory for Objects of Art and Science in Amsterdam, aimed at finding an alternative technique to standard practices in the lining of canvas paintings, in answer to a growing awareness among restorers in this field that the starch- and wax-resin lining techniques are insufficiently compatible with the properties of painting materials. The alternative technique discussed is a cold-lining method with the exclusive use of synthetic materials. Next to giving a short review of what was published in an interim report for the ICOM-conference 1972 ("Comparative Study of Conventional Relining Methods and Materials and Research towards their Improvement"), the present paper mainly elaborates on further developments which took place during the past three years. This includes the application of the cold-lining adhesive in a nap-bond system and the design and construction of a "Low-pressure cold-lining table" which makes the alternative lining method a most gentle operation.

FURTHER DEVELOPMENTS IN COLD-LINING

Particularly in the past five to ten years the number of articles and conferences dedicated to problems in the conservation of paintings on canvas has increased considerably. Some of the studies undertaken and published deal with those problems in great detail and taken together they give us a clear illustration of the circumstance that we have not yet succeeded in finding the proper way in which to retard the ageing of paintings satisfactorily. Important contributors to these studies have been, among others, G. Urbani (1) with a general survey of problems and suggestions for a program of systematic studies which may lead to the proper solutions; S. Rees Jones (2) who compiled a questionnaire sent all over the world to restorers employed in museums and privately, in order to receive detailed information on all working methods in use to-day; E. Tassinari (3) with a contribution on the physical properties and behaviour of canvas materials; B. Halström (4) who has gone into a review of adverse effects of microbial attack on painting materials; S. Keck (5) who concentrated on the behaviour of oil films; G.A. Berger (6) with studies on adhesives used in lining; R. Buck (7) who did a historical survey of stretchers and there were also significant contributions and comments by Th. Brachert (8), A. Lucas (9), U. Baldini and S. Taiti (10), R.E. Straub (11), A. Boissonnas (12) and A.J. Cummings and G.A. Hedley (13). For a general survey of painting restoration techniques credit goes to C. Wolters (14), while as recent as April 1974 a thorough and enlightening treatise appeared on what its author, W. Percival-Prescott (15) calls 'the lining cycle', a paper which deserves special mention where it draws our attention to the fact that of all measures which a restorer may take to prolong the life of a painting to the utmost, 'lining is the treatment of a painting as a whole'. And since lining is a phase which many paintings are to pass through inevitably and repeatedly our choice of methods and materials for this intervention should be 'a wise one'.

What this means is, of course, that we are obliged to stretch the cycle of lining as much as possible and that the operation itself, when it cannot be averted, should be taken care of with the greatest gentleness. This is indeed in line with all we have attempted to attain with a research program begun some six years ago, focussed on finding a proper alternative to the traditional lining techniques. Within this period we have reported on our work in three publications (16, 17 and 18). The present paper will be a review of our entire work, including the most recent developments.

In the paper which we prepared for the last ICOM-conference held in 1972 (16) we have put up a series of questions, facts and comments aimed at drawing attention to the circumstance that the

starch and even more so the wax-resin lining is actually a rather too drastic interference with the delicate equilibrium in a painting's properties, in as much as these methods either involve the use of unsuitable materials and/or go with excessive heat and pressure which in one way or another are liable to have adverse effects on painting materials. We shall not repeat the reasons and arguments for what we feel to be a strong need to basically modify the approach to lining, but we merely state again the requirements which come in their wake and which we believe to befit a gentler way of handling. Thus, whatever the nature of the materials used, they should remain reversible with regard to another lining eventually needed in the future; the use of heat should be avoided altogether; pressure in lining should be reduced considerably; the lining adhesive should not permeate canvas, ground and paintfilm alike (in other words: no 'embedding' as inherent in a lining with wax-resin or, for that matter, any other adhesive which contains wax) and therefore consolidation of paintfilm and ground should be carried out independent of lining, the latter only meant to create a bond between old canvas and lining material; it must be optional to use the selected adhesive at different rates of cohesive strength in accordance with the size and the weight and in general with the particular characteristics of a painting involved, and it is imperative that the adhesive will have proper resistance to fluctuations in temperature and humidity, that it will not lose its flexibility with time and shall not be prone to microbial attack. The last set of requirements pertains to the lining material as well.

In accordance with this we have searched for a cold-lining method while endeavouring to use only synthetic materials. Knowing that the use of synthetic materials in painting conservation has long been and still is looked upon with suspicion and hesitation by many involved in this field, we have set about designing a thorough survey in order to find out which of them could fully guarantee a safe procedure, at the same time doing away with the now widely acknowledged inadequacies of standing practices.

After years of experimental work we believe to have found a proper lining alternative and we feel confident to put it into practice. By now we have handled about fifty paintings, including out-size canvases and a substantial amount of the kind of modern canvases which responsible restorers are reluctant to touch, being aware that the established lining methods and materials are not quite compatible. The results we have had comply with the afore-mentioned requirements in every respect.

For consolidation we have experimented with Bedacryl X 122 (polybutyl methacrylate, I.C.I.) and Plexisol P 550 (an acrylic copolymer solution, Röhm & Haas). Both materials have the advantage that they can be applied in very low concentrations. We attained satisfactory results with solutions of 5 to 10 per cent. Bedacryl is dissolved in xylene and diluted in white spirit. Plexisol is both dissolved and diluted in white spirit only. Therefore we give preference to the latter, white spirit as a solvent being quite harmless to painting materials. We should add here that the quantity and concentration of a solution are, of course, determined by the condition of the particular painting for which it is used and that the restorer's sense of evaluation is a necessary attribute.

The consolidant is applied on both the facing side of the painting and on the back and, if possible, this phase in restoration is to be carried out before the painting is removed from its stretcher in order to counteract release of the inherent tensile forces. Thus the painting's canvas will not be subjected to too much contraction in as much as excessive stress on ground and paintfilm will have been reduced in advance. Evaporation of the solvent in the consolidant takes place within 24 hours. If the paintfilm suffers from blisters and/or flaking, then affected areas are treated before consolidation. In that case we prefer the use of a water-based adhesive with the addition of a thickener, i.e. the emulsion which is used for lining as well. The affected area is covered with a slight amount of the emulsion and with Melinex (polyester foil) and by gentle rubbing and manipulation of the fingers allowed to soften and resettle in its original state. The area is finally covered with a light sandbag and left to dry.

As an adhesive for lining we chose Plextol B 500 (an acrylic methacrylate copolymer emulsion, Röhm & Haas) which can be applied cold, has excellent cohesive strength and can also be employed in very low concentrations. It can be reversed without causing danger to the painting materials, it has good resistance to fluctuations in climatic conditions and it adds little weight to the total as compared to starch-glue and wax-resin. To prevent the emulsion from penetrating into the painting's canvas and groundlayer a thickener is added, e.g. a hydroxyethyl cellulose (Natrosol 250-HHR) which turns the emulsion into a butterish substance and thus prevents it from penetrating into the painting materials before polymerisation has taken place. We have also as a substitute for Natrosol experimented with vinylidene chloride acrylnitril copolymer (saran microspheres) which functions on a different principle but attains comparable results (see Appendix).

Also a common phenomenon to be dealt with is the deterioration of a painting's canvas carrier. Natural fibres are liable to be affected by certain climatic conditions and microbial attack.

That is why we rather use synthetic fabrics, i.e. polypropylene, polyester and polyamide. All are chemically inert, have great resistance to changes in temperature and relative humidity and have the unique characteristic of a low moisture absorption. They are also resistant to rot, are not subject to microbial attack and are very lightweight. Results of tests (warp and weft) may be seen in Tables 6 and 7. (For the sake of clarity we have considered it useful to reprint in this paper most of the Tables which were published already in the 1972 interim report (16)). All materials are available in different quality and type, so that linings may be accommodated following the requirements of different problems.

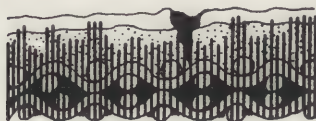
In summary a lining is carried out as follows:

1. The painting is removed from its stretcher and put face down on the working table, which, as during consolidation, has been covered with Melinex. If the restorer feels that there is a need for a facing to be applied to the painting's surface as a protection, then he will do so. Instead of employing for this purpose the commonly used pastes or adhesives, we have experimented with the above-mentioned Plexisol and gauze and we found this alternative to be quite satisfactory. Handling is eased and reversibility is improved.
2. The lining adhesive is prepared, i.e. the acrylic methacrylate copolymer emulsion (Plextol B 500) is constantly stirred while 1 percent hydroxyethylcellulose (Natrosol 250-HHR) is added. After about 5 minutes the emulsion will turn into a butterish substance. If clotting takes place the emulsion is strained before use. In our report of 1972 we noted that we used a 30% to 50% dilution of Plextol in water with the addition of 1% to 2% Natrosol as a thickener. It was applied as a thin film between old canvas and lining material. Meanwhile, however, we have realised that further reduction of the moisture content in the adhesive is desirable in view of the fact that canvas and priming of some paintings may be of a kind which react to the slightest contact with moisture and can thus indirectly cause changes in the structure of the paintlayer. Hence, further reduction of the moisture was attained through adoption of a nap-bond system in the application of the adhesive. The advantage is two-fold: We can now use the adhesive undiluted which by itself effectuates considerable reduction of the moisture content, on the other hand a nap-bond application requires a lesser amount of adhesive. For example: when Plextol is diluted 1 to 1 in water, then the total amount of moisture in the emulsion will be 75% due to the fact that Plextol contains as much as 50% water when solid. In the nap-bond lining system Plextol is not diluted, nor is it applied in a continuous film, so that the total amount of mois-

ture in the amount required is reduced by as much as 60% to 80% as compared to figures relating to the results of previous handling. This brings the amount of moisture down to a rate which is practically negligible, while sufficient cohesive strength remains guaranteed.

In order to further reduce the moisture content and increase reversibility we have, as an addition to the adhesive, also experimented with Saran microspheres instead of hydroxyethyl cellulose. Whereas hydroxyethyl cellulose acts as a thickener, Saran microspheres increase the volume through the introduction into the adhesive of minute airbubbles. The result is a decrease in peel-off strength without loss of shear strength. We intend to undertake some more testing but for preliminary results of tests see Table 9. For cross-section views of the results of these nap-bond lining techniques in comparison to traditional lining methods, see Fig.1.

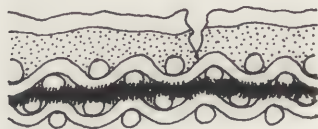
Fig. 1.



Wax-resin lining



Lining with starch



Plextol+Natrosol (film)



Plextol+Natrosol (nap-bond)

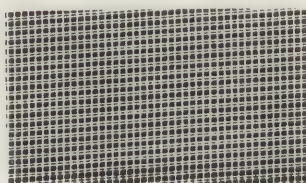
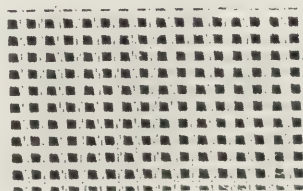
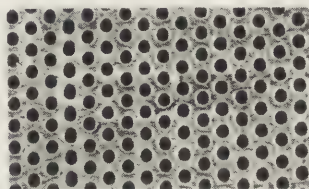


Plextol+Saran microspheres
(nap-bond)

- 3) In the nap-bond system the emulsion is not applied directly on the lining material but on a perforated nylon or plastic screen (see Appendix) with which the lining material has been covered beforehand. (One may pay special attention to the fact that in this system the adhesive is never applied on the painting's canvas). Application is carried out with a rubber spatula. When the screen is removed we perceive on the lining material a regular pattern of dotted adhesive, i.e. the dots left by the emulsion which worked itself through the perforations in the screen. Any desired rate of cohesive strength (determined in relation to size, weight and any particular characteristics of

a painting that is to be lined) may be obtained by choosing from screens with various rates of permeability and thickness, (see Fig. 2). Thus a thick screen with closely set perforations will allow for more adhesive to pass through (and hence higher cohesive strength) than a sparsely perforated, thin screen. To facilitate handling the perforated screen selected is mounted on a stretcher which will fit into the stretcher with the lining material, (see Fig. 3). After application of the emulsion the screen is removed, the painting is placed on the adhesive-dotted lining material and both are jointly put (painting face up) on a 'low-pressure cold-lining table'. a device which we specially designed and constructed for this purpose.

Fig. 2



A LOW-PRESSURE COLD-LINING TABLE

The design of this table (see Figs. 4 and 5) has been entirely inspired, or dictated rather, by the requirements specified earlier on. On the one hand it subjects the painting only to a very low and homogeneous pressure, just sufficient to effectuate good adhesion between it and the lining material while the adhesive dries out, on the other hand it allows for quick and easy evaporation of the slight amount of moisture in the adhesive. The top of the table is flat and rigid. It is also perforated so that the moisture in the adhesive between the painting's canvas and the lining material can evaporate downwards and can be absorbed by the air which circulates constantly and with turbulence through an enclosed area at the bottom of the table. The function of that closed area is that of a buffer-zone which makes the suction of the air homogeneous. The two layers of porous polyurethane sheet have a protective function, (see Appendix). The Melinex sheet covering the painting and part of the polyurethane sheet on top of it, (see Fig. 4) will prevent the air from being sucked directly through the

75/11/5-8

Fig. 3

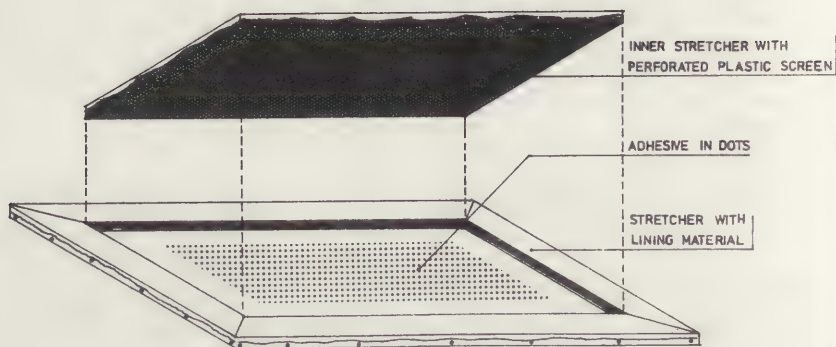
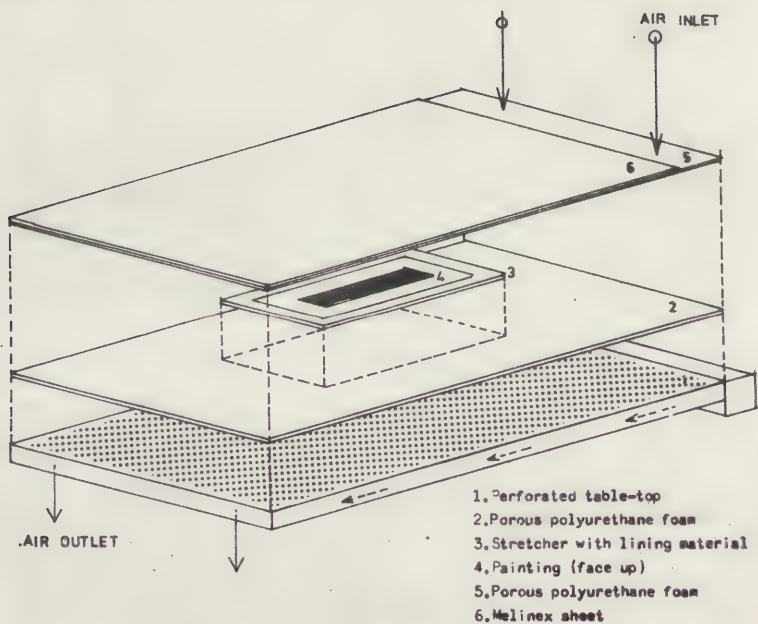
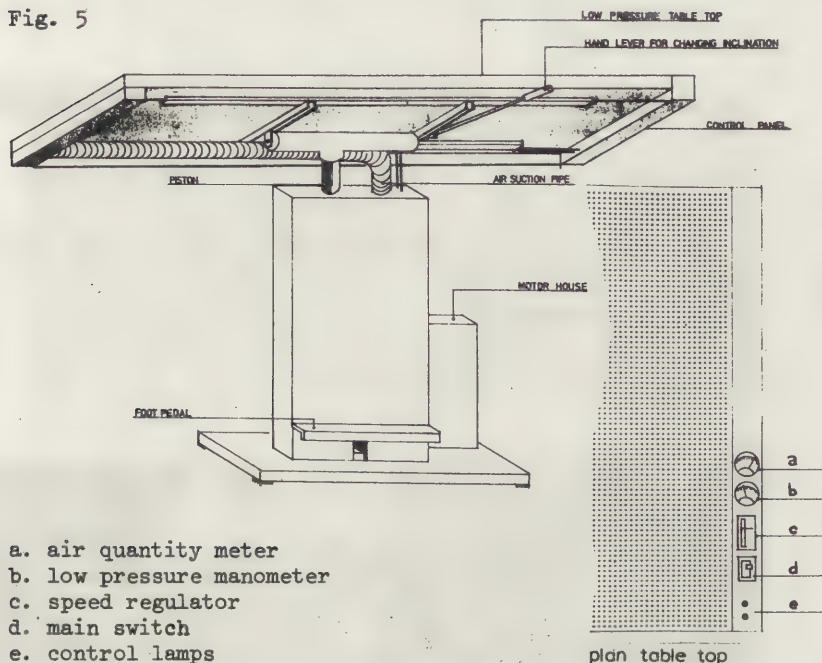


Fig. 4



painting. Air-intake occurs through a 5 - 10 cm wide margin at one side of the table-top and opposite the air-suction channel. Thus a condition of low pressure is created, with a maximum of 15 cm water-column p. sq/cm (a little more than 1 cm mercury p. sq/cm) when the motor works at full power (2800 rev. p.min.). At the right hand side of the table-top there is a control-panel on which a low-pressure manometer and a meter which registers the total air-intake p. min. Both meter-readings provide the restorer with exact data on the pressure exerted on the painting being lined and on the amount of air passing horizontally underneath the painting from one side of the table to the other. There is also a speed-control with which to regulate the amount of pressure and air-flow, (see Fig. 5).

Fig. 5



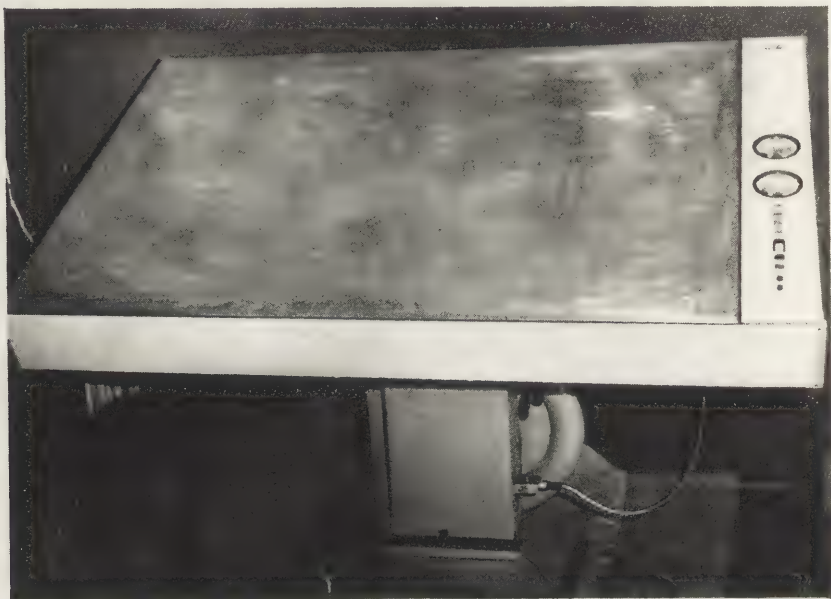
- a. air quantity meter
- b. low pressure manometer
- c. speed regulator
- d. main switch
- e. control lamps

In the experimental stage we found that the table can be used not only for the lining of paintings but also in the restoration of paper, possibly textiles as well and in museum- and studio-photography. These possibilities for multiple use have been incorporated in the construction of the table's final version. The height of the table-top can be adjusted with a foot-pedal, and with a lever the top can be put in any

75/11/5-10

desired inclination between a horizontal and vertical position. Only the drying process remains to be characterised and controlled experiments are required to define the operating parameters which influence the drying time. The air-flow rate in the buffer zone and the ambient relative humidity are expected to determine the time required for proper drying. We are proceeding with our research on these aspects, as well as on the table's multiple use.

THE LOW-PRESSURE TABLE WITH TABLE-TOP IN INCLINED POSITION



CONCLUSION

When surveying the literature on conservation techniques for paintings published during the past decade one realises that certain dangers were involved in much of what painting restorers have been doing to paintings in the past two hundred years. As far as lining is concerned, it is obvious that a traditional starch - or wax-resin lining may give good-looking results in the hands of restorers who are experienced and alert to the inherent drawbacks. But such restorers are also aware that there is no getting round the fact that the materials involved, however carefully employed, are a potential danger to a painting's properties and are of such limited durability that lining will be needed again and again. This is what Prescott (15) has called "the lining cycle" and this is also what made Arthur Lucas (9) wrote recently that "the ideal method of lining would be to line a picture without heat, with the new canvas adhering to the old without adhesive penetrating either, rather like a dry mounting paper. This sheet of adhesive should be made of material with all obvious, desirable requirements, such as stability, permanence, etc., including being easily removable; also a permanent, clear substance that could surround the painting so that it is static and everlasting, looking as on the day it was painted".

We would not claim that the cold-lining technique described in this paper gives everlasting results but it will definitely stretch "the lining cycle" in as much as its methods have induced the elimination of the use of heat, a considerably reduced increase of weight of a painting after its lining (as elaborately discussed in our report to ICOM of 1972), as well as the fact that the adhesive used may be employed at various rates of cohesive strength. Also an important feature is that reversibility of such a cold-lining is far easier than that involving the currently used methods and materials, firstly because in the cold-lining process a relatively small amount of adhesive is employed and secondly because in the nap-bond lining system 60% to 90% of the lined painting's canvas may be left free from adhesive, depending on the permeability of the screen chosen. Therefore it is most unlikely that a nap-bond cold-lining could in any way interfere with the properties of painting materials.

If a lining carried out in this manner is to be reversed one does not need to use any solvents; the lining materials can be easily peeled off without exertion of excessive stresses on the painting materials. Moreover, we found, when having reversed some of our own experimental nap-bond linings, that by far the greater part of the dotted adhesive stuck to the lining material on which it had been applied. When once having applied the adhesive to the rear of a painting we noticed at reversal that the situation was just the

other way around: most of the adhesive stuck to the painting's canvas. This means that in order to further ease reversibility the lining adhesive should indeed be applied exclusively to the lining material.

We may add here that we were particularly pleased with results in cold-lining of modern paintings with very thin and matt paintfilms. It is known to all of us that many paintings of this kind disagree with the wax-resin lining in as much as the wax which is liable to penetrate into the painting materials will easily affect tonal values and may hence violate the intention of the artist. We found that the qualities of the lining described here allow for handling of such canvases without the slightest touch of fear.

Finally, experimental work has shown us that paintings which were lined earlier with wax-resin or starch may be successfully lined again, if needed, in the ascribed manner, though on this aspect we must do some more research.

As a conclusion to this paper we restate a proposal we made in our contribution to ICOM in 1972, namely that further intensive study should be undertaken also by other restorers to determine the minimum cohesive strength required from the adhesives which are used in lining, in relevance to the size and the weight of a painting involved. Because if we let logic prevail, we may not line big and small, light and heavy paintings in one and the same manner and with adhesives of a fixed, non-adjustable cohesive strength. It must be stressed that quantifying such aspects will enhance further improvement in the practice of lining and the approach to it, which should become ever more gentle.

A P P E N D I XSPECIFICATIONS OF COLD-LINING MATERIALSPolypropylene, polyester and polyamide (lining materials):

Its fibres are chemically inert and have great resistance to fluctuations in humidity and temperature. They are designated polyolefines or olefines and have the unique characteristic of a low moisture absorption. They are also resistant to staining, do not rot, are not subject to the occurrence of mildew, cannot be attacked by insects and have a low specific gravity. For the results of tests (warp and weft) consult Tables 6 and 7.

Manufacturer of polypropylene and polyester materials used by us: Filtex Industrie, Sneek, Holland. Qualities used by us:

Polypropylene: FIA 17121 and FIA 1748;

Polyester : FIA 2322 and FIA 2324.

Manufacturer of Polyamide: (tests not included in the Tables)

De Gidts & Feldman, Postbus 7031, Amsterdam.

Qualities used by us: AH 240-Nomex and AH 500-Nomex.

Plextol + Natrosol (Adhesive + thickener): A dispersion of high-molecular acrylic-methacrylic copolymer which, in the acrylic groups, is internally plasticised.

Molecular weight: appr. 100.000;

Droplet size : appr. 1 μ (10^{-4} cm);

Amount of macromolecules in one droplet: 10^7 (10 million).

In contrast to a solution of a polymer the droplet size determines the viscosity of a dispersion independent of molecular size. In the solution the viscosity is a function of the molecular weight. This means that for the purpose of lining the water which is the carrier of the droplet should be thickened. In practice this is done by water-soluble polymers with hydroxyl - or amine side-groups which can immobilise the water molecules through hydrogen bridges. An example is hydroxyethyl cellulose (Natrosol) which we have used in our research. Other examples which could be employed are: carboxymethyl cellulose (CMC) and methyl cellulose (which are, like Natrosol, cellulose derivatives). Other possibilities are given by starch-like compounds such as dextrin, amylopectin, as well as polymers such as polyvinyl alcohol and polyvinyl pyrrolidon. Also inorganic materials (waterglass) can be used.

Plextol + Saran microspheres: Saran microspheres, Dow Chemicals, (vinylidene chloride acrylnitril copolymer) when added to Plextol create in the emulsion very minute (± 30 microns) ball-shaped air bubbles and thereby increase its volume. Thus, when applied in lining, a far smaller quantity of adhesive may be used when it is the intention to reduce the cohesive strength of the adhesive. For example: a 2% to 3% in weight of Saran microspheres added to Plextol doubles the volume of the emulsion. It is self-evident that the use of such a composition may, next to reduction of the moisture content in the adhesive, lead to a further increase in flexibility and to better reversibility.

Polyurethane sheets: The function of the porous polyurethane sheets is to facilitate a homogeneous transportation of moisture and to accommodate any irregularities which may occur in the painting's canvas, such as knots, a thick, protruding thread and the like. In the lining process we employ two kinds of sheet: on top of the table (between table and lining material), a sheet with a low compressibility (max. 0.6% when subjected to 15 cm. water-column p. cm², table's maximum capacity) and on top of the painting's surface (face up), a sheet with higher compressibility (2.5%) when employed under the same conditions. It serves as a protection and is used by us only in the lining of paintings with a high impasto which this polyurethane material will accommodate perfectly. As a final cover we use Melinex or a flexible P.V.C. sheet.

Screens: While looking for a suitable material we knew we wanted something that would be easily obtainable and inexpensive so that each sheet could be disposed of after use. There was nothing like it on the market, but we found a Dutch manufacturer (Kabor Industrie b.v., Rotterdam, specialising in perforation of plastics) ready to prepare a limited amount of flexible plastic sheets of different thickness and permeability, according to our specifications. During testing all different qualities proved to be suitable for our purpose, (cost of 50cm² about 350 Dutch guilders). We have also experimented with ordinary aluminium and other perforated metal sheets readily available and manufactured for various industrial purposes. Due to their rigidity, however, these materials cannot be handled in lining as easily as plastic materials. Moreover, the permeability of available metal sheets is mostly so high that such sheets can be suitable only in the lining of outside paintings for which a relatively high cohesive strength is required. We also made an attempt to use a nylon curtain material with an open, netted weaving. It could not be employed as it was, but after its modification through spraying with a compatible adhesive it became a useful material with relatively high permeability.

Other experiments were carried out with finely meshed nylon fabrics. The meshes in such fabric are so close together that the adhesive passing through will not form dots but will join up into a thin film of such extreme homogeneity as could not possibly be attained through any other technique in the application of the lining adhesive tried out by us. We feel that the adoption of this last film-forming technique should be considered mandatory by any restorer who feels tempted to start working in the cold-lining technique and cannot avail himself right away of suitable perforated materials. We have chosen these examples in order to show that practically any desired rate of permeability to suit various requirements in the application of the cold-lining adhesive is within reach of the 'cold liner' - all in accordance with our predilection for a lining process which leaves the restorer free to apply the adhesive with a rate of cohesive strength determined by his own choice.

A C K N O W L E D G E M E N T

I am indebted to Ir. J. Lodewijks, Director of the Central Research Laboratory for Objects of Art and Science, Amsterdam, for his encouragement towards the research involved and to other staff-members of the laboratory. I am also thankful for the assistance I had completing the testprogram from Mssrs. E. Klusman and P. de Haan (photography), Miss L. van der Loeff, Mr. Y. Hummelen and Miss D. Falvey. I am particularly grateful to my colleague J. Voskuil who was an active partner throughout most of the studies concerned and who is responsible for the presentation of this paper.

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TABLE NO. 1 Test samples relined with the commonly used methods and materials.

Peel-off test (ASTM designation D903-49)						Shear test (ASTM designation D816-55)					
No	Test sample relined with part	in	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %	apparent breaking elongation %	standard deviation (S)	variation coeff. %
1	Wax Dammar	5 2	1203	26.6	2.2	28.8	5.0	17.5	14.1	2.3	16.3
2	Wax Dammar Elemi	5 2 1	1251	147.8	11.8	41.0	5.8	14.2	15.7	1.0	6.1
3	Wax Colophonina	5 2	797	66.2	8.3	50.1	3.0	6.0	15.5	2.3	14.8
4	Wax Colophonina Ven. Terpentine	5 2 1	1822	186.7	12.4	44.2	3.3	7.3	12.2	0.4	3.3
5	Wax AW-2 Elemi	8 4 2	575	53.2	9.3	9.7	1.5	15.5	7.7	1.9	24.7
6	Starch-glue		3340	28.0	8.4	13.7	1.8	13.1	6.7	0.5	7.0

75/11/5-17

TABLE NO. 2 Test samples relined with synthetic resins and polypropylene fabric.

Peel-off test (ASTM designation D903-49)						Shear test (ASTM designation D313-55)					
No.	Test sample relined with		peel-off in grams	standard deviation (S)	variation coefficient %	shear strength in KG.	standard deviation (S)	variation coefficient %	apparent breaking elongation %	standard deviation (S)	variation coefficient %
1	Movilith DM5	1 p*	2145	332.3	16.4	23.2	9.4	40.7	11.1	2.5	22.8
	Water	1 p									
	Natrosol	4 %									
2	Plextol B 500	1 p	1320	119.5	9.1	25.6	2.6	10.1	13.8	1.8	13.2
	Water	1 p									
	Natrosol	4 %									
3	Plextol B 500	1 p	1000	48.1	7.8	25.5	1.2	4.6	11.4	1.4	12.0
	Water	1 p									
	Natrosol (on wax impreg- nated sample).	4 %									

TABLE NO. 3 Test on the increase of weight in different relining methods on a painting of an unknown artist from late 19th. century.

No.	Relining method	Weight of the painting	Weight of the new canvas	Weight of the adhesive	Weight of the painting after relining.
1	Wax Colophonia + Canvas	ca. 1010 gr/m ²	ca. 300 gr/m ²	ca. 620 gr/m ²	ca. 1930 gr/m ² incr. 91%
2	Starch-glue + Canvas	ca. 1050 gr/m ²	ca. 300 gr/m ²	ca. 240 gr/m ²	ca. 1590 gr/m ² incr. 51.4%
3	Wax Colophonia + Polypropylene	ca. 1040 gr/m ²	ca. 230 gr/m ²	ca. 470 gr/m ²	ca. 1740 gr/m ² incr. 67.3%
4	Starch-glue + Polypropylene	ca. 1070 gr/m ²	ca. 230 gr/m ²	ca. 210 gr/m ²	ca. 1510 gr/m ² incr. 41.1%
5	Mowilith DM 5 + Polypropylene	ca. 1030 gr/m ²	ca. 230 gr/m ²	ca. 80 gr/m ²	ca. 1340 gr/m ² incr. 30.1%
6	Plextol B-500 + Polypropylene	ca. 1010 gr/m ²	ca. 230 gr/m ²	ca. 70 gr/m ²	ca. 1310 gr/m ² incr. 29.7%

Although all testing strips were derived from the same painting the average weight varies because the amount of lead white and thickness of paintfilm, in each strip also varies.

TABLE NO: 4 Tests to determine the decrease in flexibility of the painting of table no. 3

		Flexibility of the painting before relining		Flexibility of the painting after relining.	
No.	Relined with	Weight in gr. per m ²	Flexibility in mNm	Weight in gr. per m ²	Flexibility in mNm
1	Wax Colophonia Canvas	ca. 916 gr.	1.6	ca. 1691 gr. increase 84.7%	49.4
2	Starch-glue Canvas	ca. 928 gr.	1.7	ca. 1375 gr. incr. 49.1%	21.5
3	Wax Colophonia Polypropylene	ca. 925 gr.	1.7	ca. 1511 gr. incr. 63.4%	19.12
4	Starch-glue Polypropylene	ca. 919 gr.	1.6	ca. 1235 gr. incr. 39.4%	9.50
5	Mowilith Polypropylene	ca. 918 gr.	1.7	ca. 1192 gr. incr. 29.8%	4.24
6	Plextol B-500 Polypropylene	ca. 923 gr.	1.7	ca. 1194 gr. incr. 29.3%	4.21

Due to limited availability of old and aged painting material the above mentioned figures are based on testing of only one single test-strip.

TABLE NO. 5 Test samples lined with a different percentage of Plextol B-500 in film and nap-bond

Peel-off test (ASTM designation D903-49)										Shear test (ASTM designation D816-55)					
No.	Test sample	1 100%	2 50%	3 25%	4 12.5%	5 6.25%	peel-off in gr.	standard deviation (S)	variation coefficient %	shear strength in KG.	standard deviation (S)	variation coefficient %	apparent breaking elongation	standard deviation (S)	variation coefficient %
1	Plextol B-500	1													
	Water Natrosol	9 2%					306	40.5	13.2	4.9	1.2	24.5	6.3	1.3	20.6
2	Plextol B-500	2													
	Water Natrosol	8 2%					357	22.3	6.3	6.3	0.7	11.7	6.9	1.1	15.9
3	Plextol B-500	4													
	Water Natrosol	6 2%					1197	89.9	7.5	9.6	0.8	8.3	8.1	0.5	6.1
4.	Plextol B-500	1													
	Water Natrosol	1 2%					1320	119.5	9.1	25.6	2.6	10.1	13.8	1.8	13.2
5.	Plextol B-500	1													
	No water Natrosol (in nap-bond)	1%					593	190.5	32.1	9.6	1.1	10.9	---	---	---

TABLE NO.6

Results of the warp tests:

Canvas	Tensile strength (kg)	Standard deviation (s)	Variation coefficient (%)
Natural	141,1	8,1	5,7
Polyester	204,6	3,6	1,7
Poly-propylene	201,0	7,4	3,7

TABLE NO. 7

Results of the weft tests.

Canvas	Tensile strength (kg)	Standard deviation (s)	Variation coefficient(%)
Natural	144,5	16,9	11,7
Polyester	165,9	5,0	3,0
Poly-propylene	143,7	2,6	1,8

TABLE NO. 8

Nap-bond lining with Plextol + Natrosol

Peel-off test (ASTM designation D903-49)					Shear test (ASTM designation D816-55)		
No.	Screen: thickness and permeability	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %
1	thickness 0.3 mm permeability ca. 6%	512	55.8	10.9	14.0	3.5	24.9
2	thickness 0.75mm permeability ca. 6%	593	43.3	7.3	17.0	3.4	20.1
3	thickness 1.0mm permeability ca. 32%	885	144.5	16.3	24.3	1.6	6.5
4	thickness 0.75mm permeability ca. 28%	1159	89.0	7.7	24.9	1.8	7.0
5	fine nylon screen	467	83.4	17.9	10.2	3.4	33.0
6	rough nylon screen	707	86.3	12.2	16.5	2.2	13.2

TABLE NO. 9

Nap-bond lining with Plextol + Saran microspheres

Peel-off test (ASTM designation D903-49)					Shear test (ASTM designation D816-55)		
No.	Screen: thickness and permeability	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %
1	thickness 0.75mm permeability ca. 6%	479	42.0	8.8	9.0	1.2	13.1
2	thickness 1.0 mm permeability ca. 6%	367	161.2	43.9	10.4	2.25	21.7

TABLE NO.10

Nap-bond lining with Plextol + Natrosol, either on lining material or on canvas

Peel-off test (ASTM designation D903-49)					Shear test (ASTM designation D816-55)		
No.	Screen: thickness 0.75mm permeability 6%	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %
1	Adhesive applied only on lining material	593	55.8	10.9	14.0	3.5	24.9
2	Adhesive applied only on the old canvas	1068	171.8	16.1	7.8	2.1	27.1

TABLE NO. 11

Nap-bond lining with Plectol + Natrosol, either on lining material or on both lining material and canvas

Peel-off test (ASTM designation D903-49)					Shear test (ASTM designation D816-55)		
No.	Fine terylene material	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %
1	Adhesive applied only on lining material	475	95.4	21.1	20.4	11.9	58.2
2	Adhesive applied on both lining material and canvas.	2125	332.2	15.6	22.6	4.5	19.7

75/11/5-26

TABLE NO. 11

Wap-bond lining with Flextol + Matrosol, either on lining material or on both lining material and canvas

Peel-off test (ASTM designation D903-49)					Shear test (ASTM designation D816-55)		
No.	Fine terylene material	peel-off in grams	standard deviation (S)	variation coeff. %	shear strength in KG	standard deviation (S)	variation coeff. %
1	Adhesive applied only on lining material	475	95.4	21.1	20.4	11.9	58.2
2	Adhesive applied on both lining material and canvas	2125	332.2	15.6	22.6	4.5	19.7

Testing was carried out on natural as well as synthetic canvases. Employed were: sheartest (ASTM Designation D 816-55) and peel-off test (ASTM Designation D 903-49), both carried out at the Vezelinstituut T.N.O., (Fiber Institute Enschede, the Netherlands) at a standard atmosphere of $65 \pm 2\%$ R.H. and at a temperature of $20 \pm 2^\circ$ C.

Test on flexibility, increase of weight and cold flow, were done at the Central Research Laboratory for Objects of Art and Science, Amsterdam, under the specified conditions.

i. PREPARATORY TREATMENT OF PAINTINGS FOR LINING
ii. A VACUUM ENVELOPE LINING METHOD
AS DEVELOPED BY W. PERCIVAL-PRESCOTT AND R. CHITTENDEN
IN THE RESTORATION DEPARTMENT OF THE NATIONAL MARITIME
MUSEUM, LONDON

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ABSTRACT

Part i of the report gives an account of the methods devised in the National Maritime Museum, London, for pre-treatment of canvas paintings before lining. The stage by stage system of stretching distorted paintings to remove bulging and cockling, to reduce cupping, and to stabilise the picture during glue removal and lining is explained. The basic procedure is advantageous whatever subsequent treatment is envisaged. Most of the structural faults caused by normal lining without preliminary treatment can be obviated.

Part ii follows the treatment of the painting through to the actual lining process, describing a recently introduced vacuum envelope system; this PVC envelope produces equal pressure on both sides of the painting, may be viewed from either side throughout the lining, and uses the hot table solely as a heat source, not as a vacuum pressure surface. It is easily adapted to paintings of many sizes. The advantages of the two systems are discussed.

(i) PREPARATORY TREATMENT OF PAINTINGS FOR LINING

Introduction

Traditionally the lining process has been regarded as a means to overcome breakdown and distortion of the painting canvas (bulges, tears, sagging, and damage caused by previous lining) and disfiguring mechanical alteration of the paint film (age cracks, cupping, cleavage, blistering, etc.) The treatments here described have developed over the last ten years in the National Maritime Museum Picture Restoration Department, as a remedy for physical defects, where the restorers looked to the original canvas support for the answer, because they doubted the value of immediate lining as the obvious solution to the problem every time.

It has become apparent that some system of preliminary treatment of the painting, before subjecting it to the rigours of the lining process, may well reduce the necessity for lining itself, while increasing the success of those linings that are made, by virtue of the original painting being prepared for the treatment it is to receive.

Condition of the Painting

In describing this technique it is assumed that the painting to be treated has already been thoroughly examined and recorded, and that for various reasons it has been found to be in a state where some form of fundamental treatment of the support can no longer be avoided.

Recording examination is included as part of the lining preparation; emphasis is placed on the use of oblique (raking) light to observe the structural condition of the surface, and of the appearance of the reverse of the painting. Throughout the prestretching stages the faced surface of the picture should be examined in oblique light at a standard position of rake.

Preparations

If at all possible, tears in the canvas are butt-joined prior to removal from the stretcher, or prior to the commencement of pre-stretching. If there is severe flaking and blistering of the paint layers, this is lightly reattached, using an adhesive compatible with both the type of the painting and the proposed lining.

system. Full impregnation of the flaking area is avoided, as this may inhibit or prevent relaxation of that part of the picture during prestretching.

It is helpful to clean a painting of dirt and varnish layers prior to stretching and lining treatment. In this way heavy varnish layers which can pull strongly on a cupped paint film, retarding relaxation during the prestretching, are removed. Also the facing and stretching papers will have a greater opportunity of close conformation with the paint surface, thus providing maximum protection, plus sufficient prestretch. Later it will be seen that one of the first stages of the pre-stretching method is to remove old lining glue (where present) which also acts as a hindrance to planal relaxation.

Facing

Certain paint types are completely unsuited to receive a facing fixative of any sort; for others this fixative must be carefully chosen to suit the paint layer; the facing fabric must be equally carefully chosen in relation to paint surface type. Our own tests have shown, for example, that in wax-resin, vacuum hot-table lining at 750 mm Hg. (where either the original canvas or the lining canvas is of a very rough and irregular texture) a fairly thick facing paper can prevent the transmission of those same underlying irregularities to the paint surface. These results can be improved still further by prestretching the painting during lining. However, if both painting and lining canvas are unstretched, and the picture without facing, maximum surface deformation may occur; this being relative to the irregularities of the supporting layers. The optimum conditions may be reached when both painting and lining canvas are stretched throughout the process, with the paper facing acting in the double role of a protective and tensioning membrane.

The choice of paper is governed by the following: (A) it must be soft enough not to cause paint surface change of any sort (e.g. facing patterns, moating) and to cushion the paint surface from the effects of other more rigid layers with which it may come into contact; (B) it must be adaptable enough to conform to all the surface irregularities of the painting; (C) it must be strong enough to take repeated tensioning of the outer margins. For these reasons three different papers are employed in this process: (1) elitoline tissue, for protective facing; (2) under-sized cartridge paper (used in lithography), for prestretching with maximum adaptability; (3) a fine strong rag cartridge paper, for firm pull at the margins.

Prestretching

The basic procedure is frequently as follows.

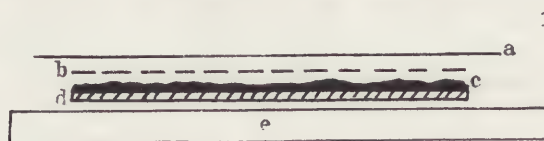
If the painting to be treated is in a weak condition and/or has a lining canvas which may be difficult to remove, a protective facing of eltoline tissue is applied to the picture surface, prior to removal from the stretcher. If the tissue has to be joined, the edges are feathered and overlapped. A facing fixative, a wax-resin mixture, is then brushed through the tissue on to the surface of the painting. In the case of an oil painting which has never been varnished, or for which a varnish-type fixative would be unsuitable, a thin water-based facing adhesive can be used. If, however, the paint layers are sound and the picture unlined this stage may be omitted. Prestretching would then be effected from the edges only.

When the facing has dried, the painting is removed from its stretcher, preserving all original parts. The back is lightly cleaned of accumulated dirt, and the folded edges are lightly dampened and ironed, or left under bar weights overnight.

A sheet of prestretching paper is cut, allowing a margin of 3" to 5" larger all round than the dimensions of the picture. The picture area is marked with pencil.

A stretching board (a sandwich of expanded polystyrene between hardboard laminates) that will not warp, of appropriate size to accommodate the stretched painting with a small margin for handling, is selected. The stretching paper is placed on it and sponged generously with water. As the paper swells, the resulting ripples are smoothed out from the centre by lightly dragging the edge of the damp sponge across the surface. This must be done with care as the paper is very weak when wet and the surface could be easily skinned or scuffed.

When the paper lies smooth and even (after about 5 minutes) and all surplus water has been removed by the sponge, the area of the picture marked within the pencil line is pasted with a prepared maize starch. It is brushed on evenly and thinly, keeping precisely to the area of the painting.



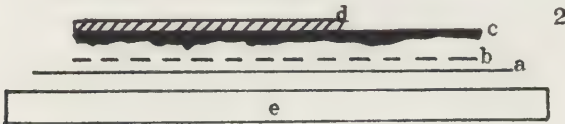
a. stretching paper, b. facing tissue,
c. painting face-up, d. old lining
survives, e. stretching board.

The picture is immediately lowered face down on to the pasted area (it is easier to allow one end down first). The back is smoothed firmly with the hands to ensure adhesion, and the painting and stretching paper are then quickly turned over on the board, before the paste starts to dry. Working from the centre outwards, a soft rubber roller is used to roll away any air bubbles and to effect total contact of the soft paper with the paint surface.

While still damp and swollen, the edges of the paper are next gently held flat and stuck down to the board with gummed paper tape, taking opposite sides in turn. The paper and painting are then left overnight to dry and pull taut.

Removal of old lining

When work on the painting is resumed, the margins are first lightly damped with a sponge and allowed to relax. The paper is then cut free from the board at its outer edges, the whole is turned over, and the paper re-taped to the board while the edges are still damp. It is then allowed to dry and tauten once more.



- d. old lining canvas during removal,
- c. painting face-down, b. facing tissue,
- a. stretching paper, e. stretching board.

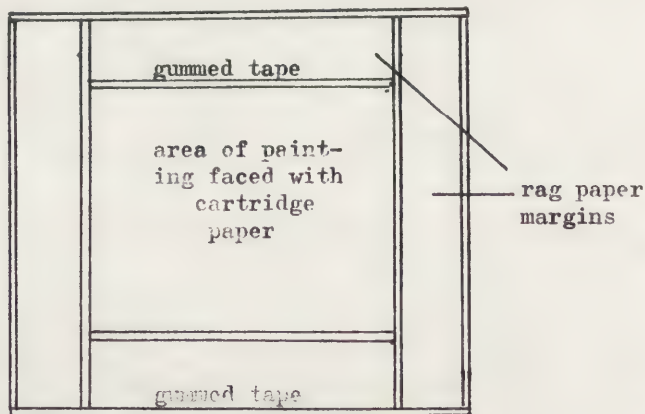
The back of the painting is now exposed for work, and it is at this stage that the lining canvas (if present) is removed, and any old lining adhesive is scraped away. For safety the glue is normally removed dry with scalpels. During this process 1" masking tape is used to secure the extreme outer edges of the painting to the stretching paper. The work is facilitated by placing the stretching board in a nearly upright position, sloping on a moveable easel. Except for very large heavy paintings, the stretching paper is quite strong enough to hold the picture in place with complete safety, the board being returned to the horizontal each night and when not in use. In this way the central back of large canvases can be correctly cleaned without damage, and without the restorer becoming unduly tired. Dust masks are worn always as animal glue dust has a high irritant factor. The dust is lightly brushed away

75/11/6-6

Care is taken to remove as much old glue as possible as its subsequent presence in the canvas layers may adversely affect the response of the canvas to prestretching and lining especially if heat and moisture are present in these processes. The back is further prepared for lining by reducing any knots or uneven threads in the canvas individually with the scalpel. Any visible damages to the back are treated at the same time.

Continued stretching

When this work has been completed, with the board once more returned to the horizontal, the picture is cut free, the cut being made just $\frac{1}{2}$ inch outside the edge of the canvas (or masking tape if present). The surplus paper remaining on the stretching board is then removed. The area of the board which will be covered by the painting is lightly sponged and the water allowed to soak in; all excess water is wiped away until the board appears barely damp. The painting is turned face-up on another surface. Four strips of heavier rag paper of the same width as the previous stretching margins, are sponged with water and allowed to swell fully. They are then attached with gummed paper tape to the protruding edges of the prestretching facing paper. The painting is returned to the stretching board, placed face-up over the dampened area, and the still damp edges of the rag paper margins are attached to the board with gummed paper tape (opposite sides first). (NB. Paper taken from a roll will have a greater contractual pull in one direction - across the width - than the other; thus the strips should all be cut across the same way to give uniform contractual pull on the painting during the pre-stretching). The paper is then allowed to dry and tauten.

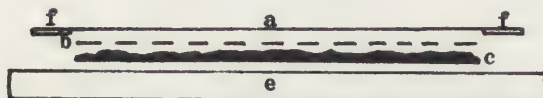


System for attaching rag paper strips during prestretching

The painting is retained in this position for about a week, the surface condition being frequently checked in oblique light.

At the end of this period, the rag paper margins are relaxed by damping; they are cut free at their outer edges; the painting is temporarily removed from the board which is redampened. Then the picture is returned face-up on to the board, and the dampened margins are pulled out taut and once more attached to the board (opposite sides first as usual). The paper is left to dry out and tauten as before for a similar length of time.

According to the response of the picture to the treatment, the process (* *) may be repeated as often as necessary, the rag paper strips being renewed about every third stretch, until the painting is judged to be ready for lining.



ff. rag paper margins attached with gummed tape
to a. stretching paper, b. facing tissue,
c. painting face-up, e. stretching board.

This is essentially a gentle relaxation process. At no stage should any extreme change of appearance be apparent. At no point is the tension of the stretching paper very high at all. Usually it is not limited to the extreme edges of the painting, but is evenly distributed by the combined facing-stretching paper over the whole paint surface. Again, minimal amounts of moisture are introduced in the process, and these are spread over a longish period. When warmth is considered necessary, this is limited to a low temperature of short duration, using an electro-thermal flexible rubber blanket; which may be applied without any hazard to local areas (where greater relaxation is needed) and to large paintings in a series of overlapping stages. Taken overall this treatment constitutes a gradual encouragement of the canvas and the paint layers below which it lies, into a position closely related to its original tensioning and consequent structural lay-out. The very slight extension of the canvas that this involves can be observed over a period of weeks by the restorer. For a point will be reached when the surface deformation, whether cockling, bulging or cupping, will have sufficient space in the underlying canvas support into which to be reaccommodated. In raking light, this 'acceptance' back into the painting, plus the

75/11/6-8

disappearance of deformities, will be seen in the more continuous nature of the surface, under its facing paper. After lining, strip-lining or impregnation there is a remarkable absence of some of the more common distracting features noted in standard lining (crushed and overlapping flakes of paint, surface wrinkles, cupping, etc.)

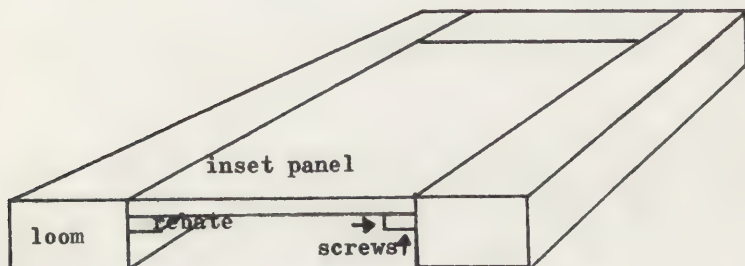
Prestretching is not a prerequisite form of treatment for every painting that apparently needs lining. Indeed every painting that apparently needs lining should not necessarily be lined. However, we have found in the majority of cases, after 10 years of prestretching practice in one form or another, that many of the undesirable conditions presented for lining, can indeed be alleviated by the preliminary stretching, in a far less hazardous fashion.

Certainly, if one considers the normal care taken by an experienced restorer in the removal of varnish and overpaint, and in subsequent retouching, often on a minute scale, and the time involved in these processes, it seems rather illogical that fundamental treatment of the painting as a whole (for that is what lining is) should frequently receive only the minimum of attention and time.

(ii) A VACUUM ENVELOPE LINING METHOD

Preparations for Lining - Loom (1)

During the prestretching, the materials required for lining are prepared. A loom is selected, its inside measurement being the size of the painting plus paper margins. A rebate is formed by screwing strips of wood round the inside, so that a stout panel (similar to the stretching board) can be inserted to lie completely flush with the top surface of the loom, fitting snugly at all the inner edges. This panel is then fixed in position by screws driven through the wooden strips from beneath.

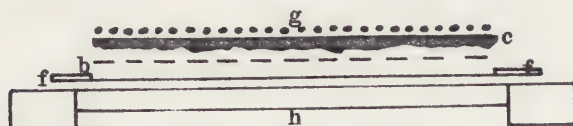


Section through panelled loom prepared to receive stretched painting

On the stretching board, the stretched painting is cut free at the inner edges of the rag paper margins, and these are discarded. The painting is laid face down on the prepared panelled loom. Fresh strips of rag paper are now sponged with water and allowed to swell to maximum size in the normal way; then they are attached to the outer edges of the facing paper with gummed tape as before, and to the upper surface of the loom. Thus, when dry, the painting is stretched across the loom over the panel, dimensions and thread count are checked again, after which the chosen lining adhesive may be applied. Whether this is applied hot or cold, with brush or roller, the application starts in the centre back of the canvas, progressing out towards the edges with regular movements, to allow the canvas to accommodate any unexpected stresses which may be set up. The adhesive layer should be as even as possible. If it is an impregnating adhesive, this stage should be carried out now, and not left to the actual lining process. Impregnation is effected

75/11/6-10

with minimum pressure (or sometimes none at all), and minimum heat (if required), working very carefully in small areas at a time, starting again at centre back, moving outwards in ever increasing circles

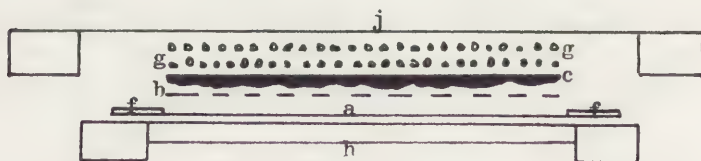


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g. adhesive layer applied to back of c. painting face-down, b. facing tissue, a+f stretching papers, h. panel set in loom.

Loom (2)

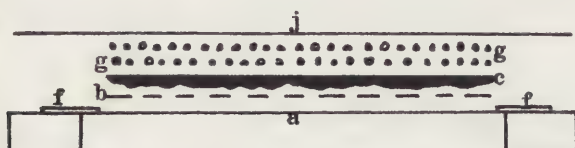
On another loom, which is large enough to completely cover the first panelled loom, the chosen lining fabric is now stretched, fully squared with the loom, maintaining an equal tension overall. The dimensions of the painting are marked centrally on the lining fabric, and the necessary area is then coated evenly with adhesive. Application is again from the centre outwards for the same reasons as above, and may be followed by impregnation if this is required by the particular lining system chosen. In this way a very even adhesive application to both canvases is achieved, plus an even impregnation, so that no guesswork is called for in the quantities of adhesive required to effect satisfactory adhesion at the contact stage. Additional even layers of adhesive may be applied to the canvas at this point if required.



5

j. lining fabric on loom, gg. adhesive layers, c. painting face-down, b. facing tissue, a+f. stretching papers, h. panel set in loom.

Loom no. 2 bearing the lining fabric is then placed over loom no. 1 and the painting. The lining fabric is stapled closely, attaching it to loom no. 1. It can then be cut free at its outer edge and loom no. 2 is lifted away. This leaves the painting and the lining fabric stretched taut on the same loom, with the adhesive coatings in contact. Finally the panel below the face of the painting is unscrewed, and removed complete with the strips of wood.



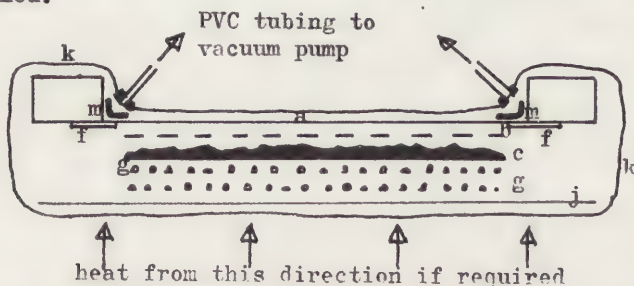
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j. lining fabric, gg. adhesive layers, c. painting face-down, b. facing tissue, a+f stretching papers, all on loom with panel removed ready for lining.

Prestretched Lining in a Vacuum Envelope

A series of holes (2mm diameter) is then cut through the paper margin only, allowing about 4" - 6" between each hole. Breathers, strips of canvas as wide as the paper margins (plus a little more, to allow them to be fixed to the inner side of the loom), are stapled in place all round the picture to conduct away the air.

The whole loom is then placed in an envelope made of PVC sheeting previously prepared to a comfortable size to accommodate it. Depending on the size of the painting, one to four vacuum ports are then cut in the PVC envelope where it is in contact with the breathers, and polythene tubing from a compressor is attached to the ports. The compressor is switched on to test for vacuum. The sides of the PVC sheeting in contact with the area of the lining are smoothed free of any wrinkles as the vacuum is established.



7

k. PVC envelope, m. breathers, a+f stretching papers, b. tissue facing, c. painting face-up, gg. adhesive

Meanwhile the hot table (or other heat source) has been brought up to an appropriate temperature level for the chosen lining adhesive. The painting, and lining fabric on the loom, in the envelope under vacuum (750 mm Hg) are then transferred to the hot table, the painting lying face up, where the vacuum and temperature are carefully maintained until adhesion is complete (usually between 10 and 15 minutes. The whole is then immediately removed and allowed to cool under vacuum, which it does in a matter of minutes, as colder air passes both sides of the envelope. Occasionally it may be necessary while the adhesive is melting on the table, to remove any small air bubbles that may be trapped between the two adhesive layers: this should be done very carefully indeed, using a soft long haired varnish brush (3") working from the centre outwards. During the setting time any small lumps or surface deformations which are undesirable, may be gently massaged through by the finger from the front to the back of the lining complex.

Advantages of the Systems

The value of this system where both painting and lining support are stretched and then lined is considerable:

1. The separating of the series of treatments of consolidation, removal of deformation, impregnation, lining adhesion, etc., enables each to receive full care and attention, and thus to produce the required results with the minimum danger to the picture.
2. The restored planal state of the painting may be retained throughout the lining treatment, and the dimensional activity of the picture canvas during the lining is thus minimised. (Similarly for the lining fabric).
3. The independent loom system allows total control at any stage of the lining process - both sides of the system may be closely observed all the time, and it may be removed from the heat source (if present) instantly, which also facilitates cooling afterwards.
4. Any type of controlled heat source may be used - IR mobile tracking systems, point source scanning systems (irons, hot air blowers), heated panels, heated blankets etc. As it is suspended independently across the loom, the surface of the lining fabric does not need to come into contact with the source of heat, even when this is a hot table (when there is a thin cushion of air in between).

5. The independent loom system allows a choice of pressure type. The use of the envelope with very low vacuum pressure is more suitable for lining paintings with surface deformation or for those liable to dimensional activity during lining treatment. Even so the prestretching method obviates the use of vacuum for anything more than maintaining overall adhesive contact and removal of air/moisture/solvent that may be present. Pressures never go above 745 mm Hg. The use of local hand, roller, or iron pressure would also be possible (in conjunction with a rigid support below).
6. As there is no pressure contact with any rigid surface, the opportunity for flattening impasto, for compression hold, producing moating, weave interference, magnification, etc. is reduced to a minimum by envelope lining where vacuum pressure is kept very, very low.
7. The freedom of both sides of the stretched lining complex offers a method where the lining support can conform to the back of the original canvas, accommodating natural irregularities in the structure, instead of falsely flattening these and thus creating surface distortion. Because of this adaptable property, the dangerous practice of rubbing down with sandpaper any irregularities on the reverse of the painting canvas (thus weakening the original structure still further) may be dispensed with. For the same reason, any unwanted surface deformity may be eased through to the reverse during setting with many of the hot setting adhesive systems.
8. All known lining adhesives (both hot and cold setting) would seem to be suited to the technique.
9. Any suitable non-rigid lining fabric (traditional or synthetic) may be used; and the prestretching process is equally desirable for use prior to marouflage techniques.
10. Striplining procedures should be preceded by stretching in the same way.
11. The method may be used for large pictures (our largest to date 84" x 109"), when the lining is carried out in zones without any danger of join marks (if heat is required).
12. In special cases where facing is impossible (where multi media have been used, or impasto is excessively high, or the painting has never received varnish, etc) the stretching may be effected from the extreme edges only.

Conclusion

The system as described above, is currently in use in the Restoration Studio here at the National Maritime Museum. But, just as its evolution and development were a long series of steps, representing experiments on every level, using the widest range of materials and techniques available to us, so its present practice continues to vary daily, according to the requirements of the picture being treated, to new materials being introduced on the market, or to old ones being withdrawn without warning. This is no great disadvantage, as thus perhaps the complacency of working with one lining method for every situation is avoided. It provided the incentive for the 1974 Greenwich Conference on Comparative Lining Techniques, an endeavour to improve our own knowledge. The intention was to refresh the attitude of the art and conservation profession to this rather neglected subject, and hopefully this will continue, under the 'Stretchers and Lining Working Group' in Venice this autumn 1975. and at future ICOM meetings.

THE EFFECT OF BEESWAX/RESIN IMPREGNATION ON THE TENSILE PROPERTIES OF CANVAS

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ABSTRACT

The load-strain curves under uniaxial tension, were obtained for the weft and warp directions, and for the direction at an angle of 45° to the warp, of 5 types of canvas. These tests were performed with the canvas samples un-impregnated and with them impregnated with a beeswax/resin adhesive mixture.

It was found that the effect of the impregnation was to introduce a new initial zone of high modulus into the load-strain curve. In addition when impregnated, the anisotropy of the canvas was greatly reduced at low strains and the samples exhibited an increased tendency to failure.

INTRODUCTION

The lining of paintings with beeswax/resin adhesive mixtures has become one of the most common forms of treatment for canvas paintings. In this technique both the original canvas and the new backing material are normally impregnated with the adhesive mixture. It is self evident to conservators familiar with this process that impregnation alters the mechanical properties of canvas. For example an impregnated canvas does not have the same flexibility as new raw canvas. But it is also clear that the tensile properties of canvas are likely to be altered by impregnation. Since lined paintings are subjected to tension when they are put back on their stretchers an understanding of these properties is important to conservators.

This paper reports on the aspects of a more general investigation of the tensile properties of canvas which indicate the effect of wax/resin impregnation on these properties.

The experiments were confined to studying new canvases, both raw and impregnated, subjected to uniaxial tension in the warp, weft, directions and at 45° to the warp and weft.

EXPERIMENTAL PROCEDURE

All the experiments were performed on a laboratory constructed

tensile testing machine. This had a fixed lower cross bar and a moving upper cross piece. The load was applied by adding weights to a simple lever system and was measured through a spring balance linked to the upper cross piece. The displacement of the upper crosspiece was measured with a dial gauge. The equipment was rudimentary but since the work was aimed primarily at comparative and not absolute measurements this was not a serious problem.

The samples were not secured to the cross pieces by jaw grips. If these had been used they would have resulted in large areas of heterogeneous strain around the grips and therefore in the sample tending to fold in on itself during loading. To overcome this undesirable effect roller grips were used. These are round bars which are free to rotate and thus allow sample rotation to take place. A loop sample must of course be used with these type of grips. In these experiments the loops were made by joining the canvas strips with 3 rows of stitching.

Strips of canvas 10 cms wide were used for all the experiments and the total loop length was between 40 and 50 cms depending on the sample. A range of 5 canvases were investigated which included a wide variety of weights and weaves. Four were linen and one cotton, the full details are given in Appendix I. These were tested in both raw and impregnated states. The impregnation was done without applying any tensile load to the canvas. Wax/resin was first brushed onto the material and this was then placed on a hot table and impregnated under vacuum pressure. The wax/resin mixture used was 90% beeswax, 10% AW2. In this way a similar thickness of wax/resin adhesive was applied as is normally used in the lining process.

When the loops had been prepared the experiments were performed in the same manner for impregnated and unimpregnated samples. The loops were fitted into the rotating grips and the load was applied in increments by adding weights to the end of the lever. Measurements of the displacement were taken after an arbitrary time of 2 minutes. From these, curves of the applied load against strain could be obtained for each sample.

Each canvas sample was tested with the tensile load applied in 3 different directions. These were, parallel to the warp threads, parallel to the weft threads and at 45° to the warp and weft threads. The applied load could be varied between 0 kg and 100 kg.

RESULTS

The results are shown in Full for two of the canvas samples which clearly indicate the general behaviour of all the samples.

Figs. 1,2 show the load against strain curves obtained for canvases A, B respectively in the unimpregnated state.

Several comments can be made on these curves. Firstly, they show the anisotropic behaviour of canvas. Under any given load, the weft direction has consistently extended less than the warp, and the warp less than the 45° inclination to the warp. The degree of difference is very large with the extension at 45° often being 10 times or more

than the weft extension.

The reason for this disparity is found in the fact that with a load applied in the warp and weft directions canvas extends by a different mechanism to that which operates with a load applied at an angle to the weft and warp. In general, under such a load canvas behaves like a trellis with the weave cross over points acting as linked joints. Under a load it therefore tends to swivel about these points in the way that a trellis opens and closes. Considerable fabric extensions can consequently be achieved with hardly any alteration in yarn lengths. The curves of Figs 1, 2 illustrate this point. Normally woven fabrics extend least for any given load in the weft and warp directions and most at an angle of 45° to the warp and weft.

All the curves of Figs. 1,2 appear to be composed of two sections an initial region of lower slope (and hence lower modulus) and a final region of steeper slope. These zones can be explained by reference to what is regarded as the generalized load-extension curve for Fabrics shown in Fig. 3:

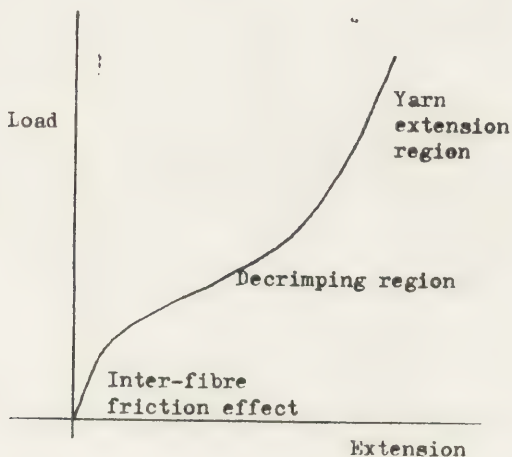


Fig. 3. The generalised load-extension curve.

This curve has three regions. An initial steep slope, which corresponds to an initial high modulus due to the frictional resistance to bending of the thread. Then once this frictional resistance is overcome there is a relatively low slope which is mainly governed by the force needed to unbend or 'decrimp' the threads in the direction in which the force is applied. Finally there is a zone of steeper slope which occurs when most of the crimp has been taken up and the fibres themselves begin to extend. In this zone the load extension properties of the fabric are almost entirely governed by the load extension properties of the yarns that compose it.

In the curves of Figs. 1,2 it is evident that the initial steep slope due to frictional resistance of the yarns to bending does not play any significant role in the canvases tested. Instead the two sections of the curves correspond to the decrimping region and to the region where the yarns begin to extend themselves. The weft direction consistently extends less than the warp because it has less crimp (due to the way that canvas is woven) and hence the yarn extension zone comes into operation much sooner. At an angle of 45° to the weft and warp the initial low modulus region is due mainly to the trellis-like deformation outlined above, as this brings the yarns nearer into the line of application of the force, they begin to be extended giving rise to the final steeper zone of these curves. The results obtained for raw canvas were therefore unexceptionable and correspond to the general behaviour of woven fabrics. It is worth noting that none of the canvases failed in any way, and that the immediate elastic recovery of the materials after the removal of the 100kg. load was very small, never more than 10% of the total strain.

Figs. 4,5 show the load versus strain curves obtained for canvases A, B when they were impregnated with wax/resin mixture. The most obvious feature of these curves is that unlike those shown in Figs 1,2 they all have three regions. The curves in fact appear very similar to the generalised load-extension curve shown in Fig. 3. From this it can be concluded that the wax resin impregnation has introduced into the load/strain curves an initial region of high modulus. This is probably due to the 'locking' effect of the wax/resin which prevents the yarns from bending and decrimping as occurred in Figs 1,2, until this 'locking' effect has been overcome. Above a load of about 15 kg. and a strain of roughly 1% this effect is in fact overcome and thereafter the canvas extends by decrimping and then yarn extension virtually as if there was no wax impregnation at all. Observation of the canvases during this transition indicated that the beeswax/resin fractured at this strain and took on an opaque white appearance. This increase in the initial modulus is not insignificant, especially when it is considered that the strains applied in the central areas of lined paintings during retouching will fall within this zone.

When the strains are plotted on polar diagrams another important factor can be seen. Figs. 6,9 show polar plots of the strains for impregnated and un-impregnated canvas at 10 kg. load and at 70 kg. load. From Figs. 6,8 which are the polar plots at 10 kg. for canvases A and B it is evident that not only does the amount of strain at this load decrease when the canvas is impregnated but the behaviour is also much more nearly isotropic. Figs. 7, 9 show the same plots for a load of 70 kg. By this load it is evident from the similarity of the curves that the impregnation has little effect on the tensile properties - the strains are very similar for the raw and impregnated samples in all 3 directions and the degree of anisotropy is the same. Consequently it can be concluded that at low strains wax/resin impregnation makes the canvas more isotropic. This phenomenon also applied to the other canvases tested, the strains at 10 kg and 70 kg are tabulated for these materials in Appendix II.

A comparison of the weft extension curves for both canvases shows that the final extension of the weft was larger for the impregnated

canvas than the raw canvas. A similar result was found with the warp extension curves of canvas B. In all other cases the extension of the impregnated material was less than that of the raw material. The reason for the extra extension of the impregnated canvas when it occurred, was because during their extension small nicks developed at the edge of the loops. These nicks weakened the sample as a whole and meant that the applied load operated over less material, they thus lead to greater extensions. The fact that these failures occurred with the impregnated canvas but not with the raw canvas indicates another effect of impregnation. That is because, particularly initially, the yarns are not free to move, weak points in the canvas cannot be compensated for by nearby yarns. This means that there is a much greater likelihood of fabric failure when it is impregnated, although failures did not in practice develop under strains of about 2.5%.

CONCLUSIONS

1. The 5 canvases tested exhibited, when unimpregnated, the anisotropy characteristic of woven fabrics. Their load-strain curves were composed of two sections, an initial low modulus corresponding to decrimping or trellis deformation, and then a region of higher modulus due to the canvas extension being governed by yarn extension.

2. The impregnation of the canvases with beeswax/resin affected the tensile properties of the canvas in 3 main ways:-

- (i) An initial region of high modulus was introduced into the load-strain curves because the impregnation led to an increased initial resistance of the yarns to bending.
- (ii) The anisotropy of canvas was dramatically reduced at low strains while the wax/resin was 'locking' the weave.
- (iii) The impregnated canvas samples had a greater tendency to failure because the yarns were not able to accommodate to 'weak spots' in the canvas.

3. In general the effects of wax/resin impregnation on the tensile properties of the canvas are desirable to the conservator. For example, since a lined painting is stretched until it is 'taut' the higher initial modulus of impregnated canvas means that lower strains will result in the desired effect. In addition the more isotropic behaviour of the canvas is evidently beneficial since it is likely to lead to more even distribution of stresses and strains in canvases. Against these two advantages must be set the increased tendency to failure of impregnated canvas. However it should be borne in mind that this occurred at strains of 2.5% or more in the weft direction and took place at the edges of the test strips. It is likely that failure in the bulk of the material would not occur until much larger strains.

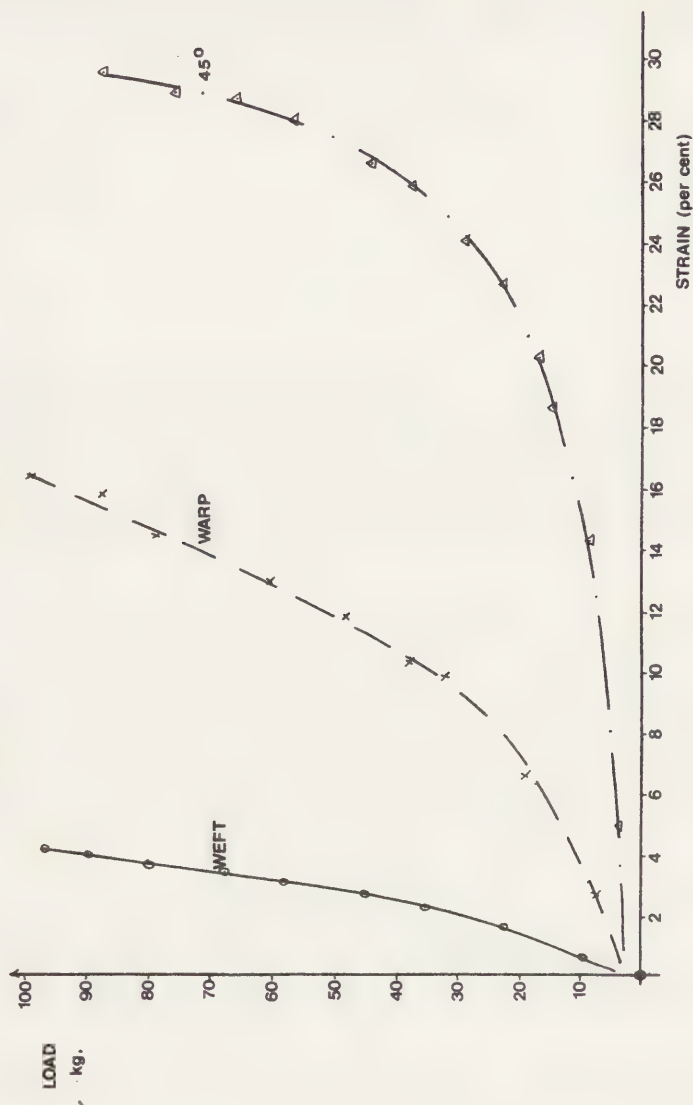


Fig. 1 The load-strain curves for un-impregnated canvas A.

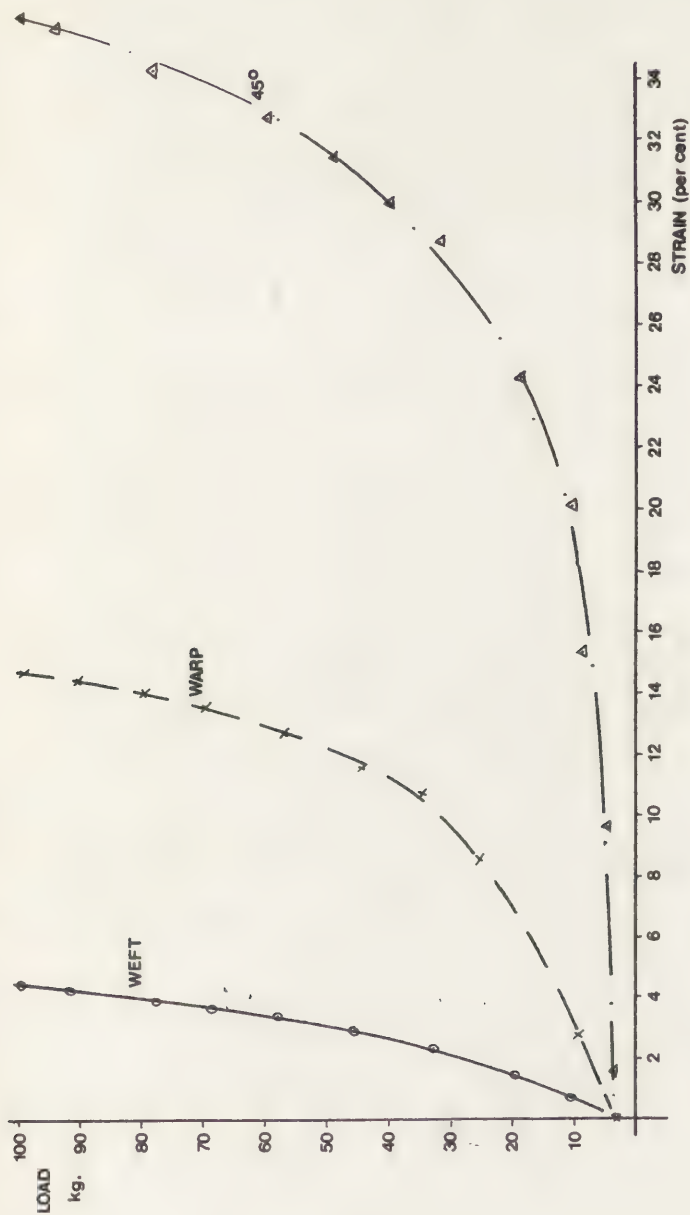


Fig. 2 The load-strain curves for un-impregnated canvas B

75/11/7-8

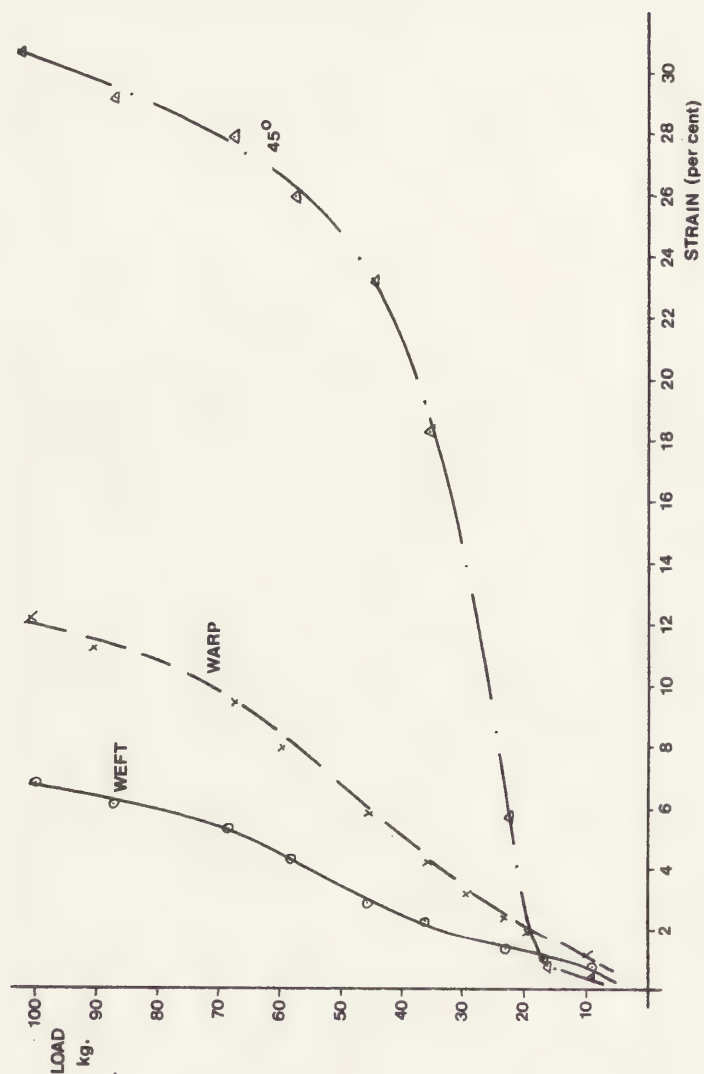


Fig. 4 The load-strain curves for impregnated canvas A.

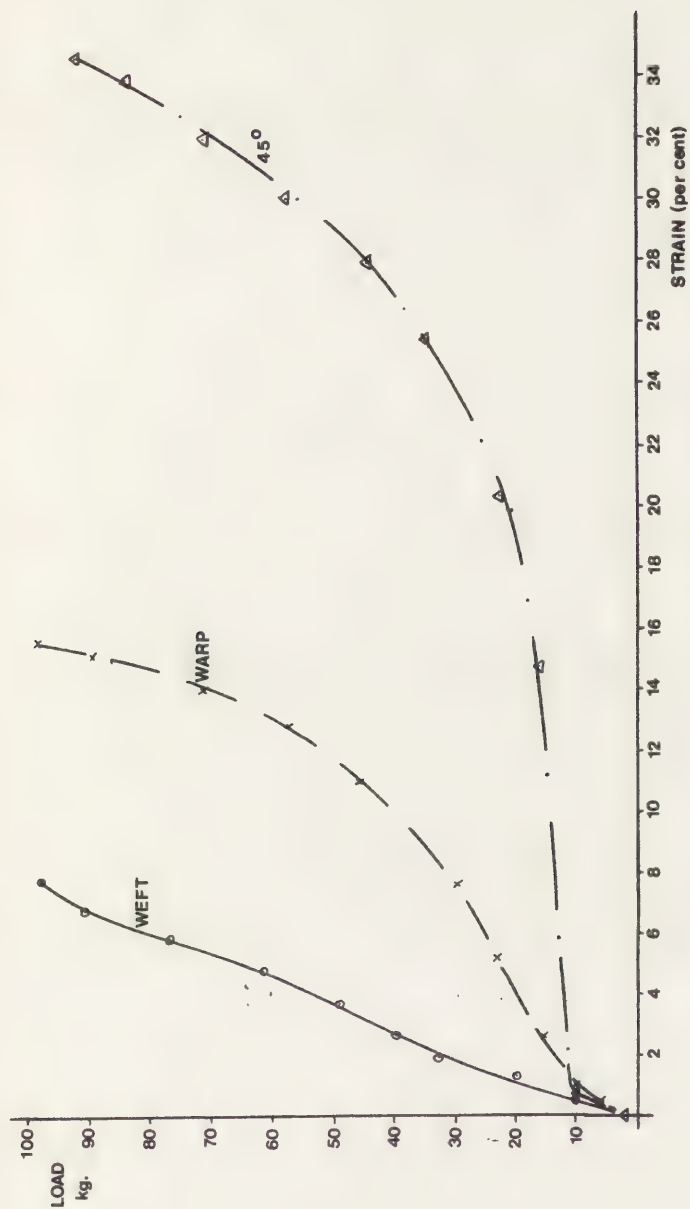


Fig. 5 The load-strain curves for impregnated canvas B.

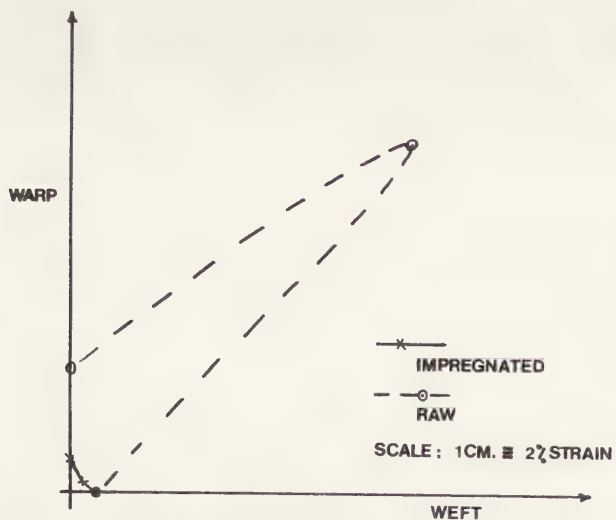


Fig. 6 Polar diagram of the strains in canvas A under a 10 kg. load.

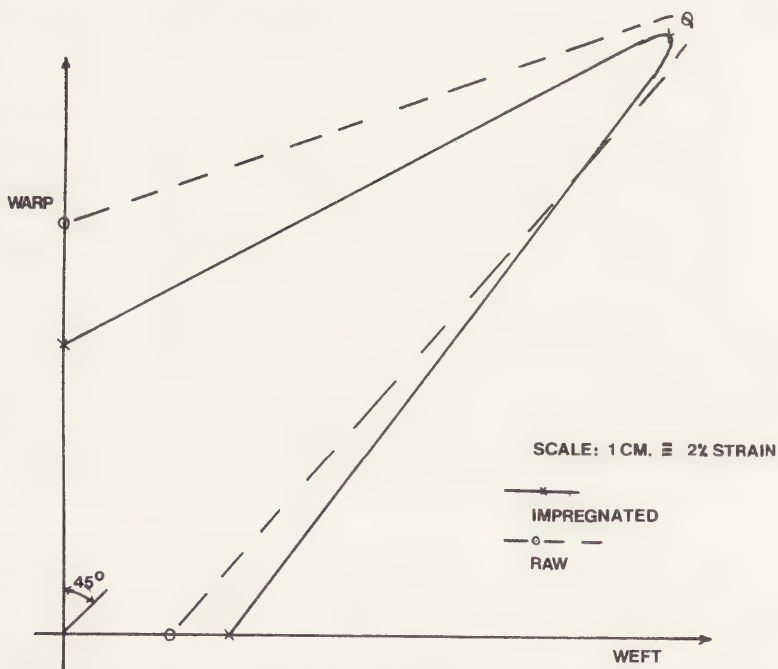


Fig 7 Polar diagram of the strains in canvas A under a 70kg. load.

75/11/7-11

Fig. 8 Polar diagram of the strains in canvas B under a 10 kg. load.

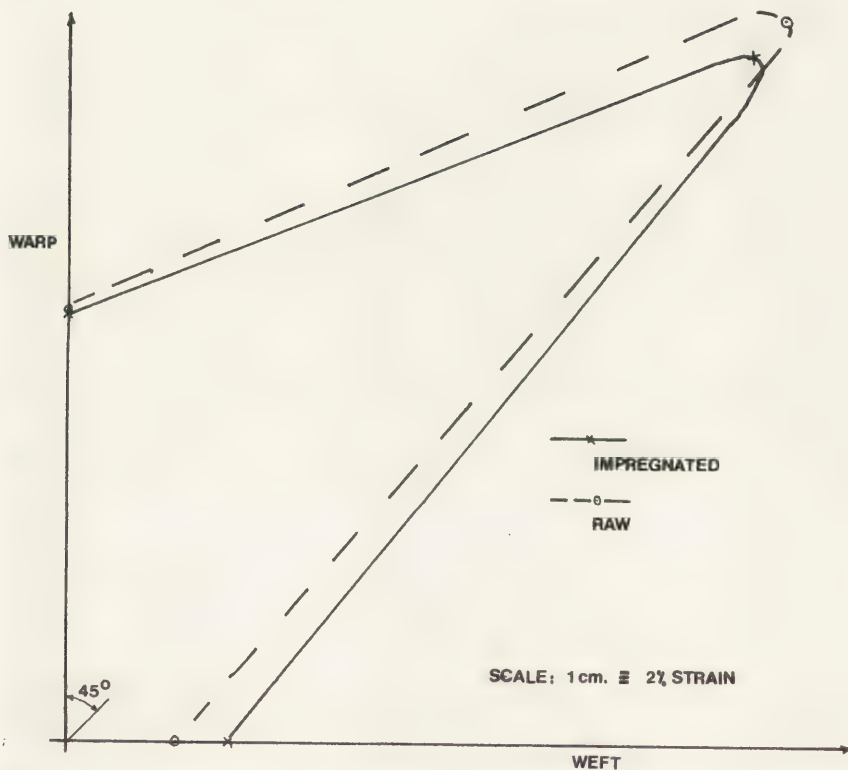
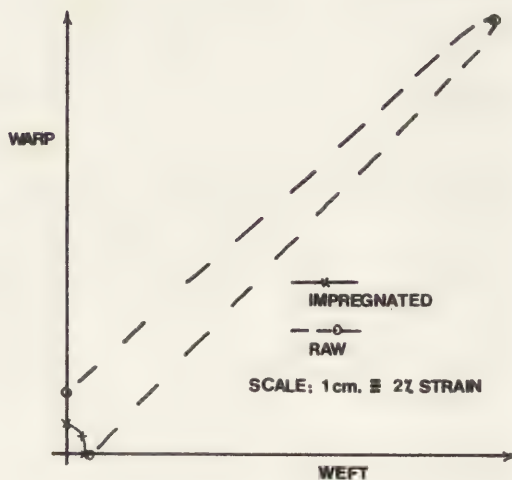


Fig. 9 Polar diagram of the strains in canvas B under a 70 kg. load.

75/11/7-12

APPENDIX I

Canvas Details:

Canvas A

Material: Linen
Warp: 13 ends/cm
Weft: 12ends/cm
Weight: 0.034 gms/sq.cm.
Trade name: 137

Canvas C

Material: Linen
Warp: 21 ends/cm
Weft: 19 ends/cm
Weight: 0.013 gms/sq.cm.
Trade name: 10

Canvas E

Material: Linen
Warp: 22 ends/cm
Weft: 18 ends/cm
Weight: 0.033 gms/sq.cm.
Trade name: 118

Canvas B

Material: Linen
Warp: 31 ends/cm
Weft: 29 ends/cm
Weight: 0.014 gms/sq.cm.
Trade name: 0

Canvas D

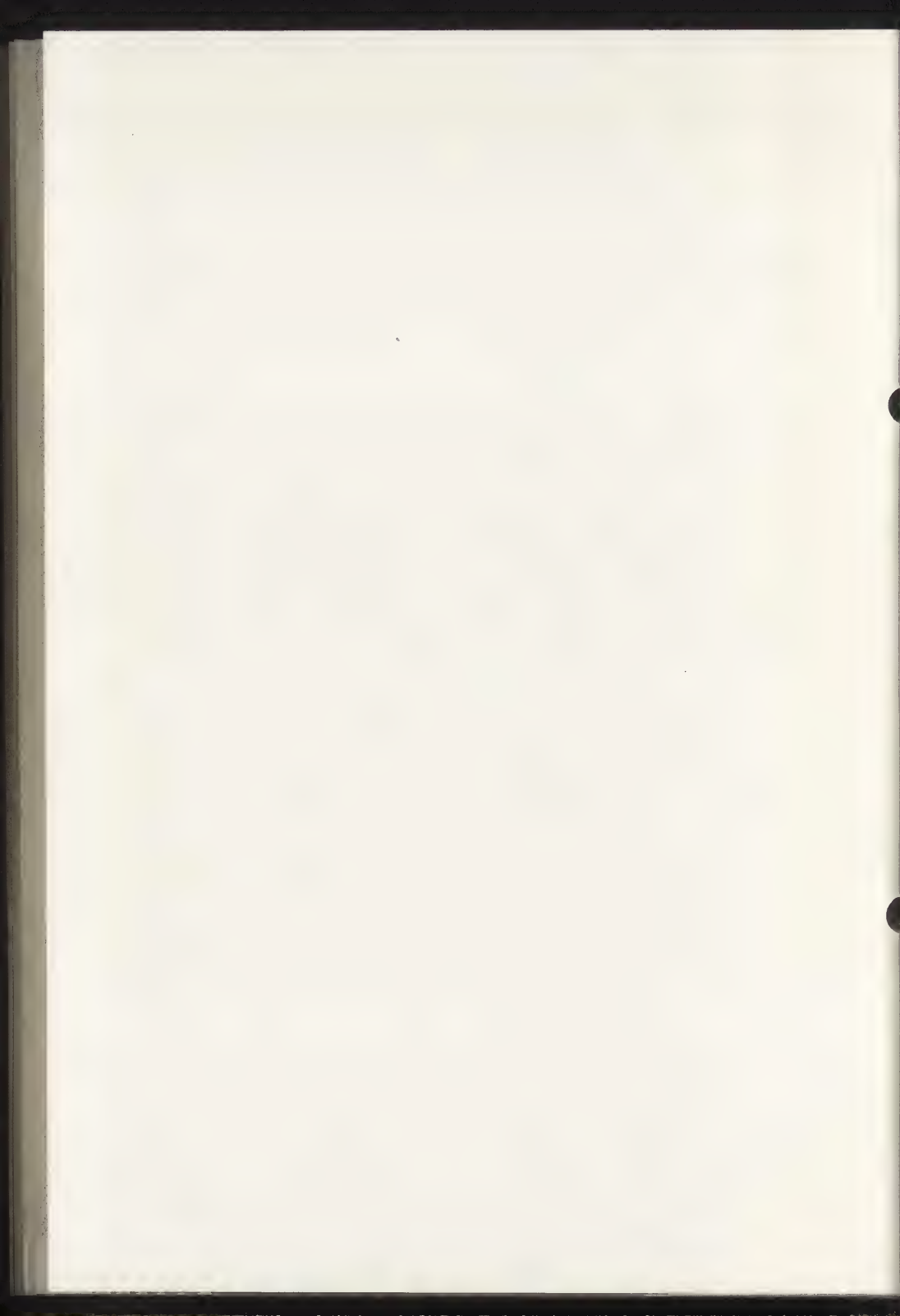
Material: Cotton
Warp: 18 ends/cm
Weft: 15 ends/cm
Weight: 0.028 gms/sq.cm.
Tradename: Duck

All canvases were of plain weave and were supplied by Robersons, Parkway, London, N.W.1.

APPENDIX II

Tabulated strains at 10kg. and 70kg. for canvases C, D, and E

CANVAS	STRAINS UNDER 10 kg. LOAD						STRAINS UNDER 70 kg. LOAD					
	RAW			IMPREGNATED			RAW			IMPREGNATED		
	Wef	Warp	45	Wef	Warp	45	Wef	Warp	45	Wef	Warp	45
C	5.4	5.4	24.0	0.45	-	0.36	11.6	-	39.0	5.4	-	20.8
D	6.0	3.6	19.0	0.65	0.98	2.62	10.7	10.4	35.0	7.9	9.0	-
E	0.3	3.5	11.3	0.3	0.65	0.35	1.8	-	28.1	4.7	10.0	20.8



THEORIE UND GESCHICHTE DER RESTAURIERUNG

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Kurzfassung

Theoretische und historische Fragen des Restaurierens sind, richtig verstanden, die Basis der Restaurierpraxis. Es muß versucht werden, Schemata zu erarbeiten, die dem Restaurator die Möglichkeit sinnvoller Auswahl geben. Die Kenntnis solcher Schemata ist Voraussetzung für die Eliminierung des Empirismus, bei dem von Fall zu Fall immer wieder neu experimentiert und das Kunstwerk gefährdet wird.

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Die Literatur ist im wesentlichen aufgeführt und verarbeitet von Cesare Chirici in seinem Buch "Il problema del Restauro", das 1971 in Mailand erschien. Besonders hinzuweisen ist auf die Bibliographie im Anhang dieses Buches. Chirici untersucht die historische Entwicklung der Restaurierung und den jeweiligen Einfluss der historischen Situation und der zeitgenössischen Kunst auf die Restaurierung. Erläutert werden nicht nur die Gemälde- und Plastik-Restaurierung, sondern auch die entsprechenden Fragen der Denkmalpflege.

Ausführliche Literaturhinweise und eine umfassende Darstellung des Themas, insbesondere unter historischen Aspekten, finden sich bei R.H. Marijnissen, "Dégradation, Conservation et Restauration de l'Oeuvre d'Art", das in französischer und flämischer Sprache 1967 in Brüssel erschien. Das zweibändige Werk enthält eine Fülle von historischen Beispielen und zeichnet sich u.a. aus durch manche auf die Praxis bezogenen Möglichkeiten, wie z.B. die mehrsprachige Konkordanz von Fachbegriffen (ein bei der Lektüre auch historischer Quellen nicht zu unterschätzendes Hilfsmittel), die umfassende, etwas kompliziert nach Themen geordnete Bibliographie.

Als Beispiel für eine mehr auf theoretische Phänomene gerichtete Betrachtungsweise, insbesondere was den wichtigen Aspekt des Zeitstileinflusses auf die jeweilige Restaurierung betrifft, seien die Publikationen von Michelangelo Cagiano de Azevedo, "Il gusto nel restauro delle opere d'arte antiche", das 1948 in Rom erschien, und J. Guillerme, "L'atelier du temps, essai sur l'altération des peintures", Paris 1944 genannt. Von Guillerme erschien im März 1965 zum gleichen Thema ein Aufsatz in der Gazette des Beaux-Arts. Michelangelo Cagiano beschränkt sich auf Plastiken und Architektur. Sein Thema und seine Sentenzen sind aber ohne weiteres zu übertragen auf alle Bereiche der Restaurierung. Der erste Satz seiner Einleitung umschreibt das gesamte Thema vorzüglich: "Il restauro è lo specchio del gusto e dell'attitudine critica di ogni epoca, ...". Thema und Grundhaltung Brandischer Restaurierungstheorie werden deutlich, die Herkunft beider von Benedetto Croce sichtbar.

Über das Thema des Zeitstileinflusses auf die Restaurierung, einen wesentlichen Aspekt der Restaurierpraxis, leider zu wenig berücksichtigt und vor allem, theoretisch kaum untersucht, habe ich in der Museumskunde 1962/2, 3 einen Aufsatz geschrieben. Diese Frage ist nicht nur formal oder ikonographisch zu verstehen sondern erreicht alle Bereiche des Kunstwerkes als Gesamtstruktur. Physische und künstlerische Struktur bedingen einander und die jeweiligen Veränderungen des einen Teils bewirken einen Wandel des anderen.

Bei allen konservatorischen Massnahmen muß die "ästhetische Überlegung gegenwärtig sein. Ebenso wie die Berücksichtigung des historischen Aspektes für die praktische Restaurierung fruchtbar ist, indem sie einen besseren Einblick in die jeweiligen Aufgaben vermittelt. Historische Übersichten über Restaurierungstechniken können also nicht nur einen "Beitrag zur Stilgeschichte, sondern auch zur Geschichte der Kunstbewertung und Kunstanschauung der verschiedenen restaurierenden Zeiten liefern. Denn der Restaurator kann sich nicht voraussetzungslos dem Kunstwerk gegenüberstellen: Stil und Sehgewohnheit der jeweiligen Zeit bestimmen die Art der Ergänzung und den gesamten restauratorischen Eingriff". Dabei kann es sein, oder besser: es ist geradezu bezeichnend, "dass, früher wie heute theoretisches Programm und Restaurierpraxis zum Teil weit voneinander abweichen". Diese Diskrepanz ist die erste Erkenntnis aus der Betrachtung der Restauriergeschichte und sie bewahrt vor einer Überbewertung der Restaurierungstheorie für die Restaurierpraxis.

In dieser Publikation wird am Beispiel der Retusche exemplarisch untersucht, inwieweit Stil und Geschmack der

restaurierenden Zeit die Restaurierung bestimmen. Es wird auch deutlich, dass die handwerklich technische Tätigkeit nicht die Beschäftigung mit irgendeiner Materie ist, sondern mit einer sehr speziellen. Der Restaurator kann diese Materie nicht behandeln, ohne nicht gleichzeitig die Gesamtstruktur des Bildes, seine Erscheinung als ästhetische Realität und historische Urkunde zumindest der Gefahr einer allgemeinen Veränderung auszusetzen.

Diese Gefahr besteht bei jeder restauratorischen Masznahme: Eine Reinigung wie ein neuer Firnis können Oberflächenglanz, Tiefenräumlichkeit und Farbcharakter des Bildes verändern, eine Übertragung auf einen neuen Bildträger kann die Oberflächenstruktur verwandeln usw. Zwischen diesen Masznahmen an der obersten Oberfläche des Bildes und seiner Rückseite gibt es keinen Eingriff, der nicht, auch wenn er nur eine einzelne Bildpartie betrifft, das ganze Gemälde verändern könnte.

Jede Zeit löst die aufgetragenen restauratorischen Aufgaben im Sinne der eigenen Kunst und Kunstanschauung. Man kann von Restaurierstilen sprechen. Am offensichtlichsten wird das bei den malerischen Ergänzungen früherer Jahrhunderte, wo ohne weiteres das alte Bild im Sinne der eigenen Zeit interpretiert wird. Die rigorosen Formatveränderungen des Barock sind gleichermaßen eine Aussage des uniformierenden Zeitgeschmacks, wie die Zurückhaltung in der Ergänzungsfrage bezeichnend ist für das archäologisch-wissenschaftliche Bewusstsein des Klassizismus. So sind auch die "Schönungen" italienischer Renaissancebilder durch Nazarener-Restauratoren zu verstehen und die anti-manieristischen Tendenzen in den Übermalungen der zweiten Hälfte des 19. Jahrhunderts, und so verbindet sich die rücksichtslose Übertragungsmanie seit dem Ende des 18. Jahrhunderts und besonders seit dem 19. Jahrhundert mit der Empfindungslosigkeit einer "glatt" malenden Epoche gegenüber Werten der Oberflächenstruktur. Gleichermäßen ist für einen grossen Bereich unserer Restaurierung heute für die Tendenz der Firnisabnahme bzw. der Reinigung, die Nähe zu impressionistischen Farbvorstellungen maszgebend und das Unvermögen, Valeurs zu erkennen.

Gewiss sind die meisten Eingriffe abhängig vom Zustand des Bildes, seinem Wert für die Kunstgeschichte oder innerhalb des Kunsthandels und seiner Bedeutung für den Kult, oder die klimatischen Verhältnisse des Ortes bedingen diese oder jene Methode. Aber es steht ausser Frage, dass theoretische Erwägungen und der historische Standpunkt die bedeutsamste Rolle bei jeder Restaurierung spielen. Diese Einstellungen richten sich nach den Anschauungen, die man vom Kunstwerk am jeweiligen Ort hat. Abhängig vom schwankenden Interesse für Zeit, Stil und Bedeutung eines Objektes wandeln sich Tendenz und Grad

der Bewahrung. Ästhetische und technologische Absichten können ausgesprochen einander ergänzen - sie können sich aber auch gegenseitig bedrängen, den Rang streitig machen und ausschließen. Im ersten Fall ist gegenwärtig zu halten, dass für das Fehlende ohnehin nur die künstlerische Wirklichkeit der restaurierenden Gegenwart ersatzweise eintreten kann. Im zweiten ist zu fragen, ob der Grad der Zerstörtheit aus den aus der Denkmalpflege übernommenen archäologisch-dokumentarischen Erwägungen tatsächlich akzeptiert werden muss. "... durch enge Anlehnung an die von der archäologischen Wissenschaft begründeten Denkmalpflege eine gewisse Gefahr erwachsen, wenn nämlich die grundsätzliche Besonderheit des Gemäldes als Bild gegenüber einem archäologischen Objekt mit mehr dokumentarischer Bedeutung nicht mehr erkannt wird. Dass zum Beispiel die Neutralretusche in der Gemälderestaurierung so geschätzt wurde, ist wesentlich aus einer solchen Verwechslung zu erklären. Hinzu kam die Stiltendenz einer Zeit, in der die Schönheit des Fragments entdeckt wurde und die Ästhetik allgemein vom Ganzen zum Fragment fortschritt. Für die restauratorische Behandlung von Gemälden ist das bedenklich, da diese Neigung ästhetische Werte schaffen bzw. suggerieren kann, die das Kunstwerk nicht enthält.

Für diese teils fruchtbare, teils fragwürdige Beziehung liefert die Restauriergeschichte zahlreiche Beispiele, zumal in der Renaissance oder im Klassizismus, wo archäologisches Bewusstsein mit denkmalpflegerischem Bemühen identisch sind. Gleichwohl liefert der Klassizismus die beste Möglichkeit, Restaurierung als theoretisches Problem zu sehen und die Bipolarität des Kunstwerks zu unterscheiden. Bis dahin war Restaurierung eine Sparte der bildenden Künste und die technische Handhabung der Aufgabe entsprechend.

Wolfgang Goetz hat in seiner Dissertation "Beiträge zur Vorgeschichte der Denkmalpflege", 1956, die wesentlichsten Fakten zu einer Restauriergeschichte zusammengetragen. Er, Stübel und Michelangelo Cagianò de Azevedo liefern wichtiges Material zu einer Restauriergeschichte. Am Beispiel der Untersuchung über die Retuschen sind diese Fakten von mir in der Museumskunde zusammengestellt worden. Hier findet sich ein umfangreiches Literaturverzeichnis mit Hinweisen auf Primärliteratur des 17., 18. und 19. Jahrhunderts und die einzig (?) wichtige Sekundärliteratur und Aufsätze zu historischen Fragen der Restaurierung.

Ein grober Überblick zeigt eine vor- und rückläufige Entwicklung innerhalb der Restaurierhistorie: Die Antike ist näher bei der Renaissance in ihrer Auffassung vom Bewahren und Restaurieren der Objekte, das Mittelalter

frei von strengen denkmalpflegerischen Erwägungen - die Liturgie ist das alleinige Regulativ für das Erhaltungswürdige - das kraftvolle Barock denkt völlig unhistorisch: Stil ist hier ein formales, kein geschichtliches Problem. Das gesamte Restaurierwesen wird noch als Kunst wie selbstverständlich in den Bereich des Schöpferischen einbezogen.

Erst der Klassizismus bringt den Restaurator, der nicht mehr unbefangen als Künstler der Aufgabe gegenübersteht, sondern als Diener. Die restaurierende Tätigkeit löst sich aus dem Verband der schöpferischen Künste. Es zeigt sich das beginnende historische Denken, dem der Sinn für den dokumentarischen Wert des Originals entspringt.

Das 19. Jahrhundert dann zeigt auch hier Versuche der Anpassung, historisierende Abhängigkeit, vielfältige Versuche, künstlerische Leere und ersten Einsatz naturwissenschaftlicher, technologisch begründeter Methoden. Eine Entwicklung, die im Prinzip bis heute fort dauert und nur ein Regulativ durch die konkrete und wahre Durcharbeitung von Restauriertheorien erfährt, die wir vor allem Cesare Brandi zu verdanken haben, dessen Untersuchungen bisher viel zu wenig bekannt sind.

Noch verborgener sind einige Hinweise in der polnischen Zeitschrift "Ochrona Zbytkow" u.a. über "Zeitstileinfluss und ästhetische Aspekte in der Gemälderestaurierung" (2/1965, S.23-34) von Heinz Althöfer. Hinzuzuziehen wäre dazu ein Aufsatz in der gleichen Zeitschrift von Josef Furdyna über die künstlerische Funktion des Restaurators (4/1970, S.243-249) und über ethische und ästhetische Probleme in der Praxis und Theorie des Restaurierens (4/1972, S.264-269) vom gleichen Autor. Den wichtigsten Aufsatz in diesem Periodikum "Über die Prinzipien der Konservation", (Meinungen und Zusammenfassung) schrieb Kazimierz Malinowski (2/1966, S.13-22). In knapper und klarer Form liefert dieser Aufsatz einen Überblick über Entwicklung und Formulierung verbindlicher Restaurierprinzipien. Die Definition dieser Prinzipien ist für den Restaurator, den Bewahrer kultureller Güter, heute eine der dringendsten Forderungen. Wie Brandi weist Malinowski darauf hin, dass Unklarheiten innerhalb der Auseinandersetzungen verschiedener Anschauungen auf der ungenügenden Analyse der Forderungen und einem Mangel einer gut entwickelten Restauriertheorie beruhen.

Verschiedene Tendenzen existieren nebeneinander: Einerseits wird gefordert, man solle das Fehlende ergänzen und das Kunstwerk rekonstruieren, damit der ästhetische Eindruck des Originals wiedererstehe. Andererseits werden gewisse Formen der Alterung, auch der Zerstörung, respek-

tiert. Grundlage der Restaurier-Theorie, so Malinowski, sei die Frage der Motivation, die unser Verhältnis zur Kunst und der Kunstgeschichte leitet. Er geht über Riegl hinaus, wenn er in unserer Einstellung dem Objekt gegenüber folgende Wertkriterien fixiert: historische, künstlerische und "nützliche". Dazu kommt der sogenannte Alterswert, der aus dem Bewusstsein der historisch-positiv gesehenen Vergänglichkeit hervorgeht. Malinowski weist hin auf die von Dvorak untersuchte Rolle der Gefühle, der Sentiments im Hinblick auf das Kunstwerk, wie z.B. Respekt vor den Vorfahren, Heimatliche - verbunden mit der Tendenz, kommenden Generationen die eigenen Erfahrungen zu übermitteln.

Der polnische Wissenschaftler wendet sich dann den Restauratoren und Theoretikern zu, die, wie Wagner, Azevedo und Althöfer, gegen eine übertriebene Verwissenschaftlichung sind und für die Wiederherstellung und Beachtung des künstlerischen Aspektes des Kunstwerkes eintreten. Daneben sieht er eine in der Tradition des Viollet-le Duc herrschende Auffassung, die für eine streng abstrakte Konservierung eintreten (Lindall, Mielke 1961, Roberto Pane 1964). Das bedeutet nicht, dass die Frage nun klar und eindeutig gelöst wäre. Die Kontroverse bestimmter Probleme bewahre ihre Aktualität, sie verlöre nur die äuszerre Schärfe und die zwingende doktrinäre Anmassung.

Einen dazwischen liegenden Standpunkt nehmen innerhalb der polnischen Restaurierung Dobrowolski und Marconi ein. Sie meinen, man solle, statt einem strikten Ergänzungsverbot zu folgen, nach dem Grundsatz verfahren, "so wenig wie möglich" zu ergänzen. Dutwiewicz sagt, der normale Kunstbetrachter verlange nicht unbedingt ein "ganz echtes" Dokument und weist hin auf unsere jeweilige Abhängigkeit vom künstlerischen und ideologischen Zeitgeschmack und findet Gründe für eine moderne Tendenz, den gegebenen beschädigten Zustand zu belassen und zu konservieren. Zugleich aber betont er die Notwendigkeit, verlorene Werte durch neue zu ersetzen. Er vergleicht die Rolle des Konservators mit der Rolle des Funkregisseurs im Bereich der mechanischen Musik.

Malinowski indes bleibt, nach Schilderung der verschiedenen Strömungen, bei dem Prinzip des bloßen Konservierens, denn es sei die einzige Basis des Konservatorenberufs. Warnend weist er auf die seit "biblischen Zeiten" hörbaren Stimmen, die dem Reiz des Vergänglichen erliegen. Dieses Bewusstsein des Unaufhaltsam-Vergänglichen, des Pessimismus und der Verzweiflung - aber auch der Zerstörung als Mittel der Bewahrung sozialer Normen und des wirtschaftlichen Ausgleichs wie bei Callais und Bataille

- dieses Bewusstsein stirbt nie ganz und rückt rhythmisch in das Zentrum der Weltschau. (Man könnte hier Bezug nehmen auf den englischen Kulturphilosophen Toynbee, der im Zusammenhang mit dem von uns bis heute falsch gesehenen Biedermeier feststellt, dass auch das absolute konservatorische Bewahren verderblich ist, wenn er sagt: "Alles bewahren, alles vernichten - eines so zerstörerisch wie das andere".) Schopenhauer und die "Existenzialisten", Spengler und Husserl sprechen von "Sein zum Tode" und von einer allgemeinen Krisis der Kultur und Wissenschaft. Dieser Suggestion sei Riegl erlegen, der nicht nur den Begriff des Alterswertes als Kriterium einführte, er habe zugleich auch diese Ansicht als höchste Stufe des Kunstschutzes angesehen. In seiner Theorie verbanden sich die pessimistischen Anschauungen Schopenhauers mit Herbert Spencers evolutionärer Tendenz zur Schematisierung der historischen Prozesse.

Der Existenzialismus liez unter Husserl's Einfluss den Menschen mit dem Wissen um seine eigene Bewusstheit die innere Zerrissenheit gewahr werden und gab ihm ein ständiges "gefühl der Leere" und der "Besorgtheit". Die Existentialisten sehen in der Vergangenheit einen Bezirk und eine Möglichkeit der Erkenntnis und des Wissens, dessen Sinn stets der Änderung und Aktualisierung unterliegt - Kriterien, die in übergeordneter kulturphilosophischer und in direkt bezogener Weise für den konservatorischen Standpunkt entscheidend sind.

Malinowski bezieht sich dann auf die Ansicht Heinz Althöfers, der, auf der Grundlage erarbeiteter historischer Fakten feststellt, dass die Restaurierung die Merkmale ihrer Epoche trägt. Trotzdem sei, aus Respekt für die Ganzheit des Kunstwerks mehr als bisher die Rekonstruktion des Fehlenden zu empfehlen, freilich unter der Bedingung, dass wissenschaftlich geprüfte Grundlagen (Dokumentation) für diese Rekonstruktion vorhanden sind.

Zwar sei jeder Restaurierfall individuell zu betrachten, dennoch formuliert Malinowski gewisse Prinzipien und Voraussetzungen für die Aktivität des Konservators: Zunächst müsse das Kunstwerk als Dokument gesehen werden. Aus diesem Grunde solle es in unveränderter Form bewahrt werden. Dann aber könne, um ein konkretes Programm für die Konservierung zu erreichen, das zu konservierende Objekt dahin analysiert werden, was zu retuschieren oder zu ergänzen sei. Diese Entschlüsse, und dies ein Wort zur Ethik des Restaurierens, mit der sich die polnischen Kollegen nahezu allein beschäftigt haben, sollten von zuständigen und verantwortlichen Personen getroffen werden.

Kunsthistoriker sollten sich mit Fragen der Restaurierung beschäftigen, theoretischen wie praktischen. (Für Restauratoren sollte es selbstverständlich sein.) Das war auch der Tenor des 20. Internationalen Kunsthistoriker-Kongresses (Studies in Western Art. Problems of the 19th and 20th Centuries, IV. Princeton University Press 1963). Unter dem Arbeitstitel "The aesthetic and historical aspects of the presentation of damaged pictures" lieferten Craig Hugh Smyth, Philip Hendy, Cesare Brandi, Richard Offner und einige Diskussionsteilnehmer verschiedene Aspekte von übergreifender, nicht auf das einzelne Objekt oder ein spezielles Restaurierproblem beschränkter Bedeutung. Die verschiedenen Gesichtspunkte bei der Ergänzung bzw. Nicht-Ergänzung von Fehlstellen werden erläutert. Hendy berichtet aus der Sicht des Museumsleiters über Fragen der Verwaltungspolitik, der Ethik und Ästhetik bei der Frage, ob der tatsächliche Zustand eines beschädigten Kunstwerkes präsentiert werden soll. Er schildert das Risiko. Er weist dann auf die Notwendigkeit, sich über die Physis der Objekte zu informieren, Grundlage theoretischer Überlegungen.

Nicht zu ergänzen oder total zu ergänzen sind Fragen des Prinzips. Antworten zu finden ist nur möglich, wenn nicht nur die technischen Voraussetzungen vorhanden sind, sondern auch die Kenntnis verschiedener Methoden, ihre Ursachen und theoretischen Begründungen. Erst dann kann die Schwäche alles Prinzipiellen, des Apodiktischen sinnvoll gemildert oder ausgeschaltet werden.

"Um die Fehler der Vergangenheit zu vermeiden, ist es wichtig, die Objekte aus historischer Sicht zu betrachten" (Richard Offner, Restaurieren und Konservieren. Zusammenfassung. Ebd. S.152 ff.) Darum fordert Richard Offner enge Zusammenarbeit von Kunsthistoriker und Restaurator. Er untersucht nochmals die Frage der Fehlstellenergänzung, der ästhetischen Forderungen des Kunstwerkes und andererseits seiner Authentizität. Alle nicht originalen Teile seien aus dem Kunstwerk zu verbannen, einzig die Konservierung des Vorhandenen sei zuzulassen.

Brandi, auf Hegel und Husserl fuszend, behandelt hier in: "Studies in Western Art" und in verschiedenen anderen Aufsätzen das Thema bis jetzt am eindringlichsten. Seine theoretischen Erörterungen werden erstmalig dem Kunstwerk in seiner bisherigen Erscheinung gerecht und stellen für die Praxis - das zeigt u.a. die Entwicklung des Tratteggio - einen überzeugenden Ansatz dar.

Seine Vorstellungen werden gleich eingangs in seinem Aufsatz über "Die Behandlung von Fehlstellen und die Gestalt-psychologie" in Studies in Western Art deutlich wenn er sagt, dasz die Behandlung der Frage von Fehlstellenergänzungen bisher immer zu verschiedenen bzw. entgegengesetzten Lösungen geführt habe, weil sie immer empirisch angefasst wurde. In Wirklichkeit sei die Lösung des Problems nur theoretisch zu erzielen. Empirische Lösungen sind notwendig. Ihr müssen sicher theoretische Prämissen von Fall zu Fall unterliegen. Aber das bedingt nicht, dasz nicht wenigstens theoretische Prämissen aufgestellt werden. Wichtig ist die Einsicht in die scheinbar selbstverständliche Tatsache, dasz es sich um ein Kunstwerk handelt, das restauriert wird. Dieses Kunstwerk ist Phänomen und Materie zugleich. Vor allem aber ist es eine Einheit, in die einzudringen wir kein Recht haben. Es sei denn, es so integer wie möglich zu konservieren bzw. nur seine bedrohte Physis zu verstärken. Integer konservieren weicht als Konzept wesentlich ab vom Restaurieren, ja, es ist entgegengesetzt. Konservieren heisst, die Integrität des Kunstwerkes absolut zu respektieren, während Restaurieren beansprucht, in die geschlossene Einheit des Kunstwerkes einzudringen und sich dem Künstler selbst gleichzusetzen.

Wenn klar ist, so folgert Brandi weiter, dasz das einmalige und in sich geschlossene Kunstwerk, mit dem wir uns beschäftigen müssen, in unsere heutige Gegenwart hineinreicht und in unserer aktuellen Gegenwart sich darstellt, dann können wir nicht beabsichtigen, sein Wesen zur Diskussion zu stellen (durch interpretierende Restaurierung), sondern es "objektiv" zu behandeln, wie es sich in unserer aktuellen Gegenwart darstellt (durch Konservierung). Alle Arbeit kann also nur darauf zielen, das Kunstwerk zu integrieren, wieder zu integrieren. Und nicht mit dem Künstler zu konkurrieren oder den Lauf der Zeit zurückzudrehen und die Geschichtlichkeit des Werkes zu ignorieren. Das heisst, wir müssen uns darauf beschränken, die Freude anderer an dem, was vom Kunstwerk übrig geblieben ist und sich uns darbietet, zu fördern, aber doch so, dasz kein Zweifel entstehen kann an der Authentizität eines jeden Teiles. Alle Ergänzung zum Beispiel kann also nur ein "Vorschlag" sein, der deutlich sichtbar ist und sich dem kritischen Urteil eines anderen unterwirft. So entstand am Istituto Centrale del Restauro das Tratteggio.

Im Zusammenhang mit seinen Überlegungen zieht Brandi die Gestalt-psychologie hinzu. Wie er sagt, als Beweis für die Methoden des Istituto Centrale del Restauro. Was ist, so fragt er, eine Fehlstelle? Im Hinblick auf die Sensibilität des Werkes eine formale und unakzeptable Unterbrechung, die wir schmerzlich empfinden. Aus dieser Störung der eigentlichen Form und dem gewalttätigen Sichein-

schieben der Fehlstelle als neue Form in einen Zusammenhang, der sich wiederum auszuschliessen versucht, entsteht die Verwirrung, die die Fehlstelle anstiftet.

Das Problem der Restaurierung, nicht nur der Fehlstellen-ergänzung, zeichnet sich hier scharf ab: Der Fehler ist zu reduzieren mit Rücksicht auf die tatsächliche Form des Kunstwerkes, d.h. nur das störende Hervorstechen des Fehlers ist zu reduzieren, nicht seine Tatsache an sich. Hier wird deutlich, wie empirisch und in seinen Resultaten immer mangelhaft die Kriterien der Neutralretuschen waren, die durch ihr Hervorstechen aus der künstlerischen Form ebenso willkürlich sind wie die Vervollständigung mit Hilfe der Phantasie.

Die so mit Hilfe theoretischer Überlegungen herausgearbeiteten Kriterien sind nun feste Punkte, die Basis für eine grosse Variationsbreite spezifischer Lösungen - und dennoch eindeutig im Prinzip, von dem sie sich ableiten.

1963 erscheint in Zusammenarbeit mit L. Vlad-Borrelli, J. Raspi Serra und G. Urbani "Teoria del Restauro" von Cesare Brandi. Das Buch enthält die wichtigsten Aufsätze Brandis, eine ausführliche Bibliographie und beispielhafte Einzelfälle aus der Denkmalpflege, der Gemälde-, Fresken- und Plastikrestaurierung. Das Buch liefert Antworten auf viele seit jeher immer wieder gestellte Fragen, es greift das Restaurierproblem an jener Seite an, die dem Kunstwerk gemäss ist und die kaum berücksichtigt wird, weil die empirisch-technologisch-naturwissenschaftliche Betrachtungsweise dominiert.

Trotz so vieler Vorzüge sind die Aufsätze Brandis ausserhalb von Italien kaum bekannt. In ihrer Nuztanwendung für die praktische Arbeit am Objekt werden sie ignoriert. Wohl als einziger hat Brandi grundlegende Fragen der Restaurierung untersucht und immer wieder klargemacht, dass unfruchtbare Polemik zumeist herrührt aus Unverständnis und dem Unvermögen, das Problem theoretisch klar zu erörtern und vom beherrschenden Empirismus zu lösen. Nur so ist eine Lösung des Problems möglich. Es ist das Verdienst der italienischen Fachleute, das Problem der Restaurierung als Problem philologischer Kritik erkannt zu haben - und erst in zweiter Hinsicht als Problem praktischer Tätigkeit.

Hier werden die Grundlagen fixiert für eine Restaurierung, die einerseits das Kunstwerk als historische Dokumentation respektiert, das heisst, die notwendige Reintegration in engsten Grenzen zu halten. Restaurierung ist nicht Schöpfung und Restauratoren sind keine Künstler: Sie sind in erster Linie Kritiker und in zweiter Techniker (Encyclopaedia Italiana 1938/48).

Aus der zentralen Forderung des Restaurierens, keine formalen und farblichen Elemente in das Kunstwerk einzuführen, entstand jene spezielle Ergänzungsmethode, die unter dem Namen *Tratteggio* bekannt geworden ist und auch in anderen Ländern praktiziert wird.

Eine zweite schwerwiegende Frage, die die Restaurierung betrifft und ein grundsätzliches Problem darstellt, ist das der Patina. Man glaubt, man könne das Kunstwerk in den Zustand zurückversetzen, in dem es der Künstler beendet hat. Patina, und das weist Brandi nach, ist technisch nicht Schmutz und ideologisch kein Romantizismus. Darum ist technologisch die Abnahme der Patina für die Lasuren gefährlich und ideologisch nicht gerechtfertigt. (Baldinucci verwendet diesen Begriff 1681). Hinzukommt, dass es ausser Lasuren original gefärbte Firnisse bereits 1261 gibt.

Diese technologischen Feststellungen haben eine Umkehr in der Meinung über das Reinigen von Gemälden bewirkt und sind ein Beispiel für die gegenseitige Stützung von Restaurierbericht, Untersuchungstechnik und Restauriertheorie. Technische Feststellung früher Lasuren und kolierter Firnisse erlaubte die Bestätigung dafür, dass Patina teil hat an der Geschichtlichkeit des Kunstwerkes. Patina, so Brandi, mindert die übermäßige Helligkeit (und Eindeutigkeit und Einseitigkeit der Materie), durch welche die ideale Verwirklichung des Kunstwerkes mehr gestört als gefördert wird. Sie muss für das Bild eine erste auszerphysikalische Spezies erreichen, um es für immer von den Zufälligkeiten der Materie zu befreien.

Nicht ohne Poesie und in direkter und nächster Beziehung zu Hegels Ästhetik wird das Kunstwerk nun auch im Bereich des materie-orientierten Restaurierbereichs überhöht. Der Hinweis auf den immateriellen Charakter des Kunstwerks eröffnet die Möglichkeit klärender theoretischer Überlegungen, die den spezifischen Charakter des Kunstwerks dem praktisch tätigen Restaurator erläutern. Romanischer Idealismus unterscheidet sich vom angelsächsischen Empirismus, bei dem auch die praktische Arbeit ästhetisch-künstlerisch und nicht technisch-naturwissenschaftlich orientiert ist. Die Tätigkeit des Restaurators wird auch beim kleinsten Eingriff enthüllen, ob im Objekt ein rein historisches Dokument gesehen wird oder seine "Artistik". Die Entscheidung dahin kann nur geleitet werden durch ein theoretisches Fundament (C. Brandi, *Il fondamento teorico del Restauro*. Boll. del'Istituto Centrale del Restauro, 50/1).

Im Lauf der Jahrhunderte hat die Auffassung, welcher Seite des Kunstwerks der Vorzug zu geben sei, geschwankt. Darum können historische Untersuchungen beitragen zur Klärung des Problems. Restaurierung ist, wie wir wissen, immer in Beziehung zur historischen Situation der Zeit zu sehen. Dabei sind bis zum 18. Jahrhundert Restaurierungen immer abhängig vom Geschmack der restaurierenden Zeit und von der Funktion des Kunstwerks geblieben. Grundsätzlich ist das auch in der Folgezeit der Fall. Allerdings gibt es in der Nachfolge unbefangener barocker Restaurierungen mit dem Klassizismus einen wesentlichen Unterschied, indem der Neo-klassizismus eine wörtliche und nicht spirituelle Wiedererneuerung der Klassik ist. Der künstlerisch-vitale Impetus, der Restaurierungen dis dahin bestimmte, ist verloren. Alle folgende Restaurierung, gleichwohl zeitstilgefährdet wie eh und je, bemüht sich spekulativ-philologisch, kritisch-wissenschaftlich. Sie löst sich aus dem Verband künstlerischer Selbstverständlichkeit und tritt in ein befangenes, distanzierendes Verhältnis zum Kunstwerk. Dort wurde durch Umsetzung ein neues Werk geschaffen, hier wird irrige kritische Interpretation geleistet.

Das alles, meint Brandi, könne zu dem Schluss führen, jede Restaurierung sei Produkt der restaurierenden Zeit und jede erarbeitete Theorie sei auch nur vorübergehend gültig zeitgebunden.

Diese Aspekte, die die theoretische Betrachtungsweise liefert, können ein Ausgangspunkt sein für die im Bereich der Restaurierung moderner und zeitgenössischer Kunst anzustellenden Überlegungen. Sie scheinen die einzige Möglichkeit zu sein, Fragen der Restaurierung zu beantworten in einem Bereich, der technologisch allein nur unbefriedigend zu bearbeiten wäre, in einigen Bezirken überhaupt nur nach theoretischen Erörterungen angegangen werden kann.

Frage der Ruinosität als ästhetische Erscheinung, Frage der Restaurierbarkeit unter dem Aspekt nur vorübergehender künstlerischer Materialisierungsabsicht, im Hinblick auf den ideologischen, bloßen Entwurfscharakter dieser Kunst, können, müssen theoretisch, dialektisch-philosophisch voruntersucht werden (Zeitschrift für Ästhetik und allgemeine Kunstwissenschaft).

THE HISTORY OF THE RESTORATION OF PAINTINGS IN POLAND
1800 - 1918

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This article deals with the conservation of paintings during the period of the loss of national independence in Poland. It concerns the years 1795-1918, when Poland was partitioned by Russia, Prussia and Austria. The loss of independence had an important effect on the preservation of historical monuments and their restoration.

National monuments and valuable objects were liable to be confiscated, seized or destroyed. The struggle for the preservation of historical monuments was connected with the movement for national independence and this resulted in its peculiar character. Thus, having no prospect of support from the government the preservation of historical monuments was totally dependent on the action of individuals, or learned, regional or other societies.

Similarly in the first half of the 19th century in Poland as all over Europe, a rapidly increasing need for people able to restore works of art was a side effect of the increasing fashion of private collections. The restoration of historical monuments was becoming an art in its own right and the practice of it became a separate skill which required more and more experience and specialized knowledge. However, that knowledge was acquired through trial and error - which led to the existence of various individual methods and techniques of improvisation as well as the creation of a pseudo-science in this field. In 1838 in the Statutes of the Technical Institute in Cracow there was a project (par. 38) to teach the restoration of paintings to the more gifted students of the School of Art. In this one can trace an attempt at a change from the system of workshop education under a master craftsman to an academic one with a set programme.

At that time the restoration of paintings consisted main-

ly of renovating, namely repainting, reconstructing, over-painting and correcting the results of previous attempts to paint over and restore. In the first half of the 19th century cleaning and washing paintings were two of the main restoration operations. Then it was wrongly believed that each art-collector ought to be able to clean his paintings himself, provided he had time. However, experience confirmed restorers in their opinion that the stronger the cleaning agent, the more dangerous it was for paintings and therefore it should be applied more carefully. Then an opinion arose that it was better to leave a picture not perfectly clean than to clean it too much. A sign of a new attitude towards restored objects could be seen in the increasing care of restoration operations, in more thorough technological investigations, and both in the increasing precision and the increasing skill in restoration operations. One can also notice, among other things, the development of the documentation of completed works of restoration. Besides the previous method of recording information on restoration on the actual object itself, there came into being a new form of documentation, namely in the reports of a committee of restorers who were especially summoned together to restore the more important works of art, for example the restoration of Wit Stwos' (Vitus Stos) altar in St Mary's Church in Cracow. The above-mentioned reports contained fairly detailed descriptions of the state of preservation, technological investigations as well as techniques and further suggestions. On the grounds of these reports it is possible to reconstruct fairly precisely the methods and means used in restoration at that time. Some of these reports were published in the contemporary daily press. They influenced public opinion in favour of the preservation of historical monuments and increased respect for restorers and their work.

The development of cataloguing historical monuments, reproduction techniques in addition to regarding a work of art as a document significantly influenced the development of restoration documentation. The regarding of historical monuments as documents caused a distinct differentiation in restorers' work between original and later supplements as well as in noticeable alterations; while in restoration documentation it resulted in a detailed recording of the state of preservation before restoration and in clear listing of all alterations and reconstructions. At the same time the opinions about restorers and role of restoration became more precise. The foundation of the Institute of Archaeology and Fine Arts formed by the Cracow Learned Society and of a special Committee for Restoration of Monuments within this Institute was an example of anxiety of the society over the preservation of works of art.

This anxiety was enhanced by the Fire of Cracow in 1850 which proved a tragedy for the City's monuments. The Committee consisted of the most important Cracovian art experts of those days, distinguished for their knowledge of both artistic and technological problems such as J. Łepkowski, T. Zebrawski, K. Kremer to name but a few. The Committee for the Restoration of Monuments took care of movable monuments only, without interfering with the work of the 'C.K. Central Kommission zur Erforschung und Erhaltung der Baudenkmäler' (The Central Commission for the Discovery and Maintenance of National Monuments), which took care of architectural restoration. Thus the (former) Committee filled the gap existing in the Austrian sector of partitioned Poland - in respect of the disregard of the state of movable monuments. The suspension of the Learned Society by the Austrian Government (from 1852-1858) consequently stopped the work of the Committee for the Restoration of Monuments in the same period.

The practical and theoretical conservation that took place in Europe at this time reflected itself immediately on partitioned Poland. For instance Karol Soczyński, in his work entitled 'The Renovation of Pictures, Figures and Wood-cuts ...' (1840), used Italian, French and German sources. When Soczyński was writing his work it was his ambition to publish a restoration manual. This is indicated in the content of the work, which deals with the following problems: what renovation consisted of, how it could be learnt; the cleaning of paintings; the removal of varnish; the washing of paintings; the conservation of paintings; the relining and transfer of paintings; the straightening of wood-supports; the fixing of detached regions; pointing; the preparation of varnish; and figure-cleaning. Soczyński's book was one of the few extensive and detached works on this subject in the years 1800-1840. In 1845 a translation of Lucanus's 'Precise Instructions for Cleaning and Restoring Pictures' was printed. Five years later (1850) the Cracow Learned Society published its 'Instructions to Serve as A Guide in Archaeological Research ...' containing information concerning the theory and practice of restoration. This was a complete independent and original Cracow product and was definitely not inferior to the best European achievements in the field of restoration. The work of art-restorers such as: Józef Cholewicz; Józef Meyer, a chemistry lecturer of the Jagiellonian University; Ludwik Łepkowski; Walery Elias; L. Lindquist - did not differ from similar work abroad. In the discussed period the change in the intensity of polish was still a pretext to decide whether a painting or gilding would be accepted and was the grounds for its correction through repainting. For example, while restoring the miraculous picture of Jesus belonging to the

Augustinian Order in Cracow, Janikowski repainted it so thoroughly that he had to produce a new picture to calm his employers. In the second half of the 19th century the surface removal of dirt from paintings became a secondary operation in restorers' work though it was still considered to be of importance. It was characteristic of the period that various 'cleaning waters' (mostly from abroad) came into the market and they did more harm than good.

In August, 1851 the first exhibition of restored easel-paintings took place. It was held in the 'Goldsmith's Chapel' in the Cracow Franciscan church. Portraits of Cracow bishops restored by Józef Cholewicz were exhibited there. In the sixties polemics concerning methods of renovation of pictures were published in the columns of the daily press.

In the second half of the 19th century the level of Polish restoration concepts can be found in numerous articles by various authors published in the Polish press of those days, as well as in the books of Władysław Łuszczkiewicz (a painter and an art-historian), namely 'Instructions for the Upkeep of Catholic and Orthodox Churches And the Preservation of Their Historical Monuments' (Cracow 1869) and 'A Manual for Those People Engaged In The Upkeep And Restoration of Churches And Church Equipment' (Warsaw 1887). Due to these books he gained the reputation of an outstanding specialist in the field of restoration and preservation of works of art. It can be stated then that anything that was new in restoration was known in Poland (e.g. Prof. Pettenkofer's problem of varnish regeneration, etc.).

In the years 1860-1900 much work was carried out in the field of wall-paintings - discovery of old paintings completely covered by more recent ones and restoration works. The restoration of wall-paintings was subordinated to architectural works. That subordination was caused by the fact that the management of the work as a whole was a rule in hands of the architects. The following were the most distinguished restorers of wall-paintings in southern Poland: Józef Mikulski, who among other things restored the polychrome of St Mary's chapel in the Carmelite church in Cracow; Izidor Jabłoński, a professor in The School of Fine Arts who restored paintings in the Holy Cross Chapel; Krukowski and Bakowski renovated paintings in the Wawel Cathedral in Cracow. Jan Kanty Zieliński restored wall-paintings in St Barbara's Church; Teofil Kopystyński among other things restored the polychrome of the Lubomirski Chapel in the Dominican Church as did Franciszek Tuch in the Church of the Holy Cross in Cracow. It is interesting to study the methods applied in those works. The renovation of Wit Stwosch' altar (1866-

1871) devoted to Mary was the biggest renovation work in the field of polychrome sculpture. The most outstanding experts in the art of those days took part in that particular work e.g. Józef Łepkowski and Władysław Luszczykowski, the painter Jan Matejko, and the architect Teofil Zebrawski, who translated the manuscript of the monk Teofil into Polish. The main guide-lines of the restoration can be summarized in the following quotation: 'although the work of the great master should be respected and should not be either corrected or freely supplemented at the same time there is no use in conserving deterioration, whereas if we are able to reproduce faithfully and accurately the intentions of the artist we should endeavour to do so without eradicating the artist's own style' (The minutes of the proceedings and activities of the Committee for the Restoration of Monuments, on 12th February 1866, Archives of St Mary's Church, Cracow.).

As far as concerns the field of easel art conservation Bronisław Adamowicz should be mentioned. He was a painter who advertised in the contemporary press the services of his studio in the renovation of old paintings on canvas, wood and metal. It was opened on February 20, 1860.

In 1873, in the Austrian partition Learning Academy, which was founded in the middle of the 19th century, appointed a Committee to study the history of art in Poland. It was the main task of the Committee to take care of matters concerning the preservation of monuments and to complete an inventory of such. Nevertheless, a Groups of Restorers of West Galicia with its seat in Cracow and of East Galicia with its seat in Lvov (founded in 1889) contributed most of all to restoration. This was because their members were outstanding experts in conservation and restoration and had great influence on conservation movement in the other parts of partitioned Poland.

The preservation of historical monuments in the Russian partition totally depended on the society. In 1906 the Society for the Preservation of Historical monuments was founded in Warsaw. It advocated love and respect for the Polish culture and its past as well as advocating the preservation of historical monuments. It carried out propaganda, cataloguing and restoration work. The Society rendered enormous services to Polish historical monuments during the First World War.

In the years 1900-1918 it can be seen how the concepts concerning the preservation of monuments, e.g. among others those of J. Ruskin, A. Riegl and M. Dvorak were accepted and adapted in Poland and the extent of their influence on the restoration of paintings. That period

was rich with opinions preserved in the contemporary daily press and magazines.

As early as the end of the 18th century artistic, educational and historical values were considered to be most important in a historical monument. At the beginning of the 20th century a concept of antique value arose, which gradually became the main principle of conservation. At the time when the principle was partly disappearing Józef Muczkowski wrote: 'The cult of antique value protects a historical monument from man's interference. It prevents any additions, any removal of alterations caused by nature, and any harsh cleaning of historical monuments which would change its hitherto existing form'. Historicism originated the concept of preserving historical monuments in the state in which restorers found them, no matter whether all of it goes back to the same period and has the same artistic value or not. However, circumstances make it inevitable to abandon such strict principles and to accept a compromise. Thus, at the first conference of The Lovers of Native Monuments in Cracow Dr Aleksander Czolowski talked about a mid-way tendency between conservation and restoration.

The first congress of The Lovers of National Monuments, which took place in Cracow in 1911, provided a lot of information concerning both theory and practice in the field of conservation and restoration of monuments. A year later a complete edition of the proceedings of the congress was published in a book form.

It was not the first congress of Polish restorers and conservationists since in May, 1909 for instance in Warsaw there was a conference of restorers organized by the local Society of Preservation of Historical Monuments. But it was the first congress organized on such a large scale. One hundred people attended the conference, representing all the three Partitions. It was the aim of the conference for the conservation officials to come to an agreement with the clergy, restorers and lovers of the past on matters concerning principles of preservation of historical monuments and their restoration as well as to exchange various practical experiences. The character of that congress can be specified to some extent by subjects of the papers presented there: e.g. 'The Contemporary State of Knowledge Concerning The Conservation of Monuments' by J. Muczkowski; 'The Attitude of Art Museums to The Conservation of Historical Monuments' by S. Tomkowicz; 'Conservation of Old Paintings' by J. Makarewicz, etc.

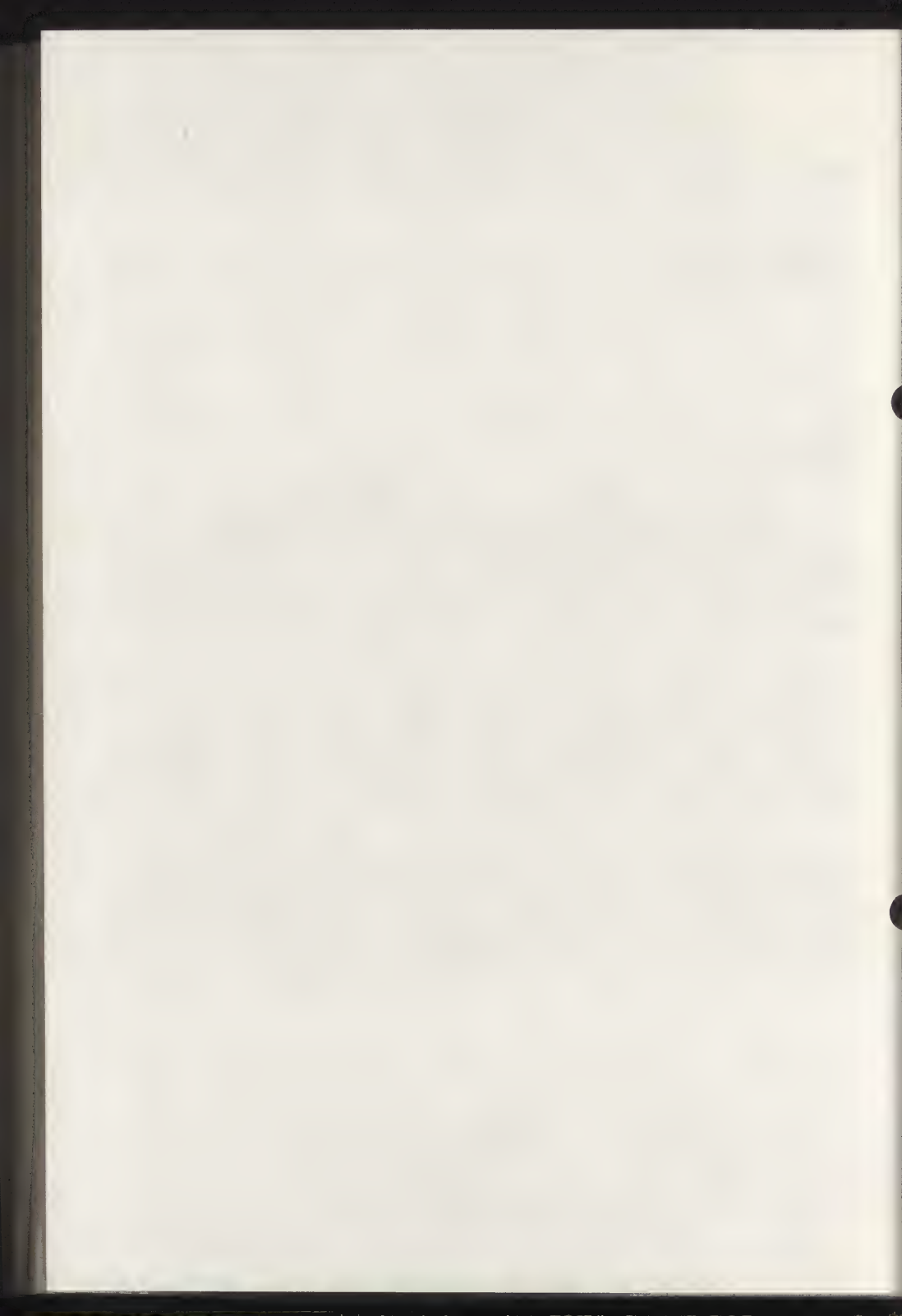
Immediately before the outbreak of the First World War appeared a book by Józef Muczkowski entitled 'The Preser-

vation of Monuments'. Its author wanted a) to answer the question 'How one should preserve' and b) to suppress the disagreement between the clergy and restorers concerning the preservation of works of art. At the same time Muczkowski pointed out the fact that as one cannot cure all diseases with the same medicine, it is impossible to conserve and restore everything using the same method.

The development of theoretical aspects of conservation was paralleled by more and more active and effective actual restoration both of wall and easel painting. Many paintings unknown till then were discovered and then restored. Thus, for instance in 1912 Juliusz Makarewicz discovered wall-paintings in the library, cloister and the Cistercian Church in Mogiła.

The war of 1914-1918 increased the problem of restoration of historical monuments, a lot of which were relentlessly destroyed during that time. But even during those years there were many actions undertaken in the field of conservation of historical monuments. Among them should be mentioned the foundation of a voluntary 'Social Guard of Historical Monuments' in Cracow at the end of 1915. The Guard had to protect works of art from destruction during the war. Stanisław Fabiański, a painter, became its chief and Franciszek Turek, a painter and a restorer, was his successor. The Guard was supported by the city and university, and its members got special badges. The first actions of the Guard were to prepare anti-fire equipment and to hoist white and blue-striped flags on 36 Cracow monument-buildings as warning signs against bombing.

The First World War put the conservation of paintings in a very difficult situation. Thus when Poland regained independence in 1918 there was a necessity to rebuild not only industry, agriculture, the school-system, etc., but also the restoration of monuments.



GESCHICHTE DER ENTDECKUNG DER MITTELALTERLICHEN RUSSISCHEN
MALEREI IN DEN ARCHIVALISCHEN SAMMLUNGEN ANFANG DES XX.
JAHRHUNDERTS

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Das wissenschaftliche Interesse an die mittelalterliche russische Malerei entstand schon in den 40er Jahren des XIX. Jahrhunderts, lange Zeit aber wurde sie aufs Geratewohl untersucht, denn fast die gesamten alten Ikonen und Fresken waren viel später übermalt. Das Auffinden des wahren Gesichts dieser Malerei geschah erst Anfang des XX. Jahrhunderts. Zwischen 1905 und 1915 wurden die Denkmäler der nationalen Kunst zum Gegenstand der leidenschaftlichen Begeisterung und des Sammelns. In diesem Zeitraum fand die Entdeckung der altrussischen Malerei hauptsächlich auf privater Anregung statt und konnte deshalb auf keine entsprechende Weise entwickelt werden. Nach der Oktoberrevolution nahm der Staat das Ausfinden und die Restauration der Denkmäler der altrussischen Kunst in seine Hand. Genau in diesem Zeitraum wurden die aller-ältesten und wertsten Kunstwerke entdeckt. Zur gleichen Zeit bildeten sich die Hauptprinzipien der wissenschaftlichen Restauration heraus und wurde der Grund zur wissenschaftlichen Geschichte der altrussischen bildenden Kunst gelegt.

Die Untersuchungen und die Veröffentlichungen der Kunstwerke der altrussischen Malerei blieben lange Zeit hinter dem Tempo ihrer praktischen Entdeckung zurück. Zum Teil war es mit dem Mangel an Geldmittel, Papier, Druckmaschinen und Druckern in der Zeit des Ersten Weltkrieges und in den Jahren der Revolution und des Bürgerkrieges in Russland zu erklären.

In den privaten Sammlungen der führenden Kunstforscher, die sich unmittelbar mit der Entdeckung und dem Sammeln der nationalen Kunstwerke beschäftigten, sowie in den Staatlichen Archiven waren viele wertvollen Materialien aus der Geschichte der altrussischen Malerei und des Prozesses ihrer Untersuchung vorhanden. Das sind vor allem die unveröffentlichten Schriften der bekannten Kunstforscher: Notizen, Artikel, Entwürfe zu den unbeendeten Schriften, Stenogramme, Leitsätze zu den Berichten.

Einen wichtigen Abschnitt bildet das private Material: Erinnerungen, Tagebücher, Briefe, und schliesslich die offizielle Dokumentation: Berichte der wissenschaftli-

chen Sitzungen und Kommissionen, Rechenschaftsberichte der Museen und Expeditionen, Niederschriften der Restaurationsprozesse, Register und Inventarlisten, Aktennotizen und Dienstkorrespondenz. Im Labor für Restaurierung und Konservierung des Museumsgutes wird zur Zeit auf der Basis dieser Materialien das Buch "Neue Entdeckungen der altrussischen Malerei" zum Druck vorbereitet, das im allgemeinen 1975 beendet sein soll. Gleichzeitig bereitet man ein Sammelband von Briefen zu diesem Thema mit Kommentar und den Artikeln über Autoren vor. Das Labor ist auch an der Vorbereitung der mehrreihigen und vielbändigen Ausgabe "Berichten über die Geschichte der altrussischen Malerei" interessiert, wo die bedeutendsten und wertvollen archivalischen Dokumente veröffentlicht werden können. Zur Zeit analysiert man die praktische Möglichkeit und die organisatorischen Prinzipien dieser Ausgabe.

HISTOIRE DE LA RESTAURATION EN ESPAGNE

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L'histoire de la restauration et de la conservation des oeuvres d'art en Espagne a fait l'objet de très peu d'études. La connaissance qu'on en a est révélatrice du comportement de l'Espagnol face à son patrimoine artistique et culturel et nous pouvons observer comment il passe de l'abandon primitif à un sens croissant de ses responsabilités à l'égard des oeuvres héritées de ses ancêtres. L'histoire de la restauration nous permet de mesurer l'évolution de l'appréciation de l'oeuvre d'art.

Le manque d'informations sur la restauration que nous constatons dans les archives s'explique de différentes manières. Jadis, il n'était pas jugé nécessaire de faire une étude minutieuse des traitements auxquels avait été soumise une oeuvre en mauvais état; le restaurateur était peu enclin à expliquer en quoi avaient consisté ses interventions. Nous pouvons dire qu'il était réfractaire à ce genre d'information. Il visait tout spécialement à réaliser une restauration presque imperceptible. Les méthodes n'avaient pas d'importance; le jugement ne portait que sur le résultat. Par ailleurs, les notes et les rapports étaient peu compatibles avec l'atmosphère de mystère créée autour du métier. On attribuait au restaurateur une profonde connaissance des secrets d'atelier. Il est évident que le spécialiste avait tout intérêt à entretenir ce mythe.

Les informations trouvées dans les archives sont, pour la plupart, des arrêtés essentiellement administratifs, qui contiennent très peu de renseignements sur les traitements appliqués aux oeuvres.

Il nous est impossible de déterminer un moment de l'histoire où aurait commencé la restauration. En effet, le simple fait de prendre soin d'une oeuvre précieuse est déjà en soi un traitement de conservation et nous savons qu'on s'occupait déjà du bon état des monuments et des oeuvres d'art aux époques les plus reculées.

Jusqu'à la Renaissance, nous constatons qu'en général, l'artiste restaurateur se comporte, avec l'oeuvre d'art mutilée, comme un conquérant. Malgré son admiration pour elle, il lui manque le respect fondamental qui devrait le pousser à la préserver comme témoignage du passé. Il n'a pas conscience de ce que l'oeuvre d'art est aussi un document historique.

A la Renaissance, on commence à distinguer la valeur historique de la valeur artistique de l'oeuvre d'art, mais cette vision n'est pas universelle et une foule de données nous prouvent un manque de respect à l'égard des oeuvres anciennes.

Il nous faut attendre le XVIIIe siècle pour que la restauration devienne une science et une technique au service des oeuvres d'art. A partir de là, les premiers critères modernes de restauration voient le jour.

...

L'histoire de la restauration, sujet tellement vaste vu la variété des éléments qui y interviennent (elle comprend l'architecture, l'archéologie, la peinture, la sculpture, les documents bibliographiques, les tissus, etc.), avec des problèmes différents et donc des solutions et des évolutions différentes, commence en Espagne dans le domaine de l'architecture.

A l'origine, quand un édifice avait besoin de réparations ou d'ajouts, ils se faisaient dans le style dominant de l'époque. Nous avons ainsi la "Chambre Sainte" d'Oviedo, restaurée en style roman au XIIe siècle; les piliers du transept de la cathédrale de Burgos, restaurés en style plateresque au XVIe siècle et la façade de la cathédrale de Pampelune, restaurée en style néo-classique au XVIIIe siècle. Malgré tout, la conception moderne de la restauration semble errer dans bien des périodes du passé. Relevons les aspirations architecturales ("sicut Toletó fuerat") de l'humble roi des Asturies, Alphonse le Chaste; la restauration "à la romaine" d'une partie de l'aqueduc de Ségovie par le moine Escobedo au XVe siècle et les réparations de l'Alhambra, à l'époque des rois catholiques, avec le concours d'artistes maures "si hábiles qu'on distingue difficilement le refait du primitif".

Les divers courants de la restauration jettent leurs bases à la moitié du XIXe siècle. Les nouvelles théories passent de France en Espagne et donnent lieu à d'énormes polémiques aboutissant à la naissance de plusieurs écoles: l'Ecole pour la Restauration, l'Ecole contre la Restauration (suivant les théories de Ruskin et de Viollet-le-Duc) et les Sous-Ecoles pour la Conservation et les Ruines. La lutte entre elles fut acharnée, provoquant de vives controverses dont de nombreux textes rendent compte.

Le début du XXe siècle voit apparaître les premières dispositions espagnoles en matière de restauration des monuments. En 1915, les monuments sont déclarés nationaux (théâtre romain de Mérida) ou d'une valeur architecturale et artistique (château de Calahorra-

Grenade) ou encore, s'ils ne sont pas compris dans l'une des déclarations officielles, il leur est reconnu une importance manifeste (Alcazar de Tolède).

En 1918, le règlement des commissions provinciales des monuments historiques et artistiques déclare qu'ils sont tous placés sous la surveillance de ces commissions. Aucune restauration de monuments appartenant à la nation (Etat, Eglise, Conseil général, Municipalité) ne peut être entreprise sans le contrôle de l'Etat. Le ministère de l'Instruction publique, conseillé par le comité des constructions civiles, doit nommer un architecte qui est chargé du monument et prépare le projet de restauration. Pour que les travaux soient autorisés, ce projet doit être approuvé par l'académie royale des Beaux-Arts de San Fernando. Ces dispositions remontant à 1918 n'énoncent pas clairement la législation espagnole sur les droits et devoirs de l'Etat à l'égard des restaurations effectuées dans le domaine de la propriété privée.

Outre ces lois de caractère général, les premières années du XXe siècle voient apparaître une série de dispositions pour défendre et conserver divers monuments du patrimoine national; elles font ressortir le souci croissant à l'époque de sauvegarder le patrimoine monumental espagnol. C'est ainsi que, par exemple, en 1913, se crée l'association des "Amis de l'Alhambra" qui a pour but de promouvoir la restauration de ce monument et d'obtenir les crédits ou les dons nécessaires.

En 1926, un décret-loi est promulgué par le roi en vue de la protection, de la conservation et de l'accroissement de la richesse artistique.

La loi de défense du patrimoine artistique national est approuvée en 1933. Elle avait pour objectif principal le recensement des monuments qui, vu leur caractère artistique ou historique, méritaient la protection et la tutelle de l'Etat. En 1949, il est créé le Service de protection des châteaux. En 1953, un accord est conclu avec le Saint-Siège à propos de la conservation, de la réparation et, éventuellement, des transformations des temples, des chapelles et des bâtiments ecclésiastiques déclarés monuments nationaux, historiques ou artistiques. En 1958, la Direction générale des Beaux-Arts publie le catalogue général des restaurations de monuments réalisées au cours des vingt dernières années; celles-ci s'élèvent à un total de six cent quarante-neuf monuments et vingt-six ensembles monumentaux.

En 1961, la même Direction crée le Service national d'information artistique, archéologique et ethnologique, dont la mission est également de dresser l'inventaire artistique et archéologique du pays.

En 1973, cette Direction crée encore l'Ecole de Restauration des Monuments en vue de la formation d'architectes spécialisés dans cette branche.

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L'histoire de la restauration en matière de peinture, de sculpture et d'archéologie suit une voie parallèle dès l'aube du XXe siècle, mais ses débuts sont très différents, la restauration picturale l'emportant sur tous les autres domaines.

Les renseignements dont nous disposons sur les méthodes et les matières utilisées, au cours de l'histoire, par les restaurateurs espagnols de peintures, sont très minces. La plupart des techniques et des formules couramment employées ont dû se transmettre oralement ou être gardées secrètes dans les ateliers. Toutefois, il nous serait sans aucun doute possible, en consultant les archives des musées, des cathédrales et des églises, de trouver une grande quantité de renseignements qui nous aideraient à reconstituer une histoire plus concrète de ce que fut à ses débuts la restauration picturale en Espagne. Ce serait un travail de longue haleine, mais extrêmement intéressant.

Les mentions concernant la restauration de peintures dans les textes antérieurs au XVIIIe siècle traitent fréquemment de nettoyage, mais elles sont si laconiques qu'elles ne nous éclairent que très peu sur les techniques et les produits employés. Par conséquent, elles ne nous permettent pas de nous faire une idée précise de ce que fut la restauration des oeuvres d'art avant 1700. Il en découle toutefois que l'artiste restaurateur se sentait peu d'obligations vis-à-vis de l'oeuvre qui lui avait été confiée. L'intervention subjective n'était pas condamnée. C'est ainsi qu'en restaurant une oeuvre, on la corrigeait. Adapter l'oeuvre ancienne à sa propre époque paraissait être la règle pour l'artiste restaurateur, bien que parfois, il adaptât également son intervention à l'objet traité.

Le XVIIIe siècle occupe sans aucun doute une place privilégiée dans l'histoire de la restauration. Désormais, une tendance se dessine clairement: la restauration tend à se mettre au service de l'oeuvre d'art. Par ailleurs, un élément extrêmement significatif apparaît: la restauration devient un problème technique. Le recours au rantoilage se répand fort et deux nouvelles techniques interviennent, la transposition et le parquétage.

En Espagne, ces courants de restauration sont mis à l'épreuve à la suite du terrible incendie de la forteresse-palais de Madrid en 1734. Une collection si importante d'oeuvres picturales (patrimoine, à l'époque, de la maison royale) y était conservée que, pour les sau-

ver des flammes, on coupa les toiles au couteau avant de les jeter par les fenêtres, ce qui les détériora considérablement.

L'événement fournit au peintre Juan Garcia de Miranda l'occasion de montrer ses dons de restaurateur de tableaux anciens. Parmi les oeuvres que cet artiste restaura, il y a lieu de mentionner spécialement les *Ménines* ou tableau de la Famille, de Velasquez; l'Adoration des Mages, de Rubens; *Vénus et Adonis*, du Titien, et les *Deux Vénus couchées*, du même peintre. Ce travail si délicat lui fut confié par Philippe V, qui, reconnaissant ses aptitudes, fit de lui son peintre attitré.

Sous le règne de Charles III, le peintre de la cour, Andrés de la Calleja, poursuivit la difficile tâche entreprise par Miranda. Son travail, tout aussi réussi et constant, dut néanmoins être très limité.

Sous le règne de Joseph Bonaparte, c'est Mamel Napoli qui fut nommé restaurateur, mais aucune source sûre ne nous permet de lui attribuer la moindre restauration. Apparemment, cet artiste se limita à veiller sur la masse de peintures qui s'accumula dans le bâtiment du Rosario après la suppression des couvents (décret-loi pris par Napoléon à Charmartin le 4 décembre 1808). Les tableaux déposés là, en provenance de diverses régions du pays, étaient mal emballés; beaucoup étaient sans châssis et, en outre, le bâtiment n'était pas prévu pour abriter pareille quantité d'oeuvres d'art. Les tableaux furent dès lors très endommagés. Parmi les plus abîmés, signalons les huit oeuvres que Murillo avait peintes pour l'Hôpital de la Charité de Séville, fondé par Miguel de Mañara.

Lors de la retraite précipitée des troupes françaises, les plus belles peintures du palais royal de Madrid et toutes les oeuvres marquantes venant des provinces furent remises dans des caisses. Nombreuses furent celles qui furent exposées très solennellement au musée du Louvre. Peu après, en 1815, le traité de Paris restituait la plupart d'entre elles à l'Espagne.

Parmi les oeuvres emportées à Paris pour constituer le musée universel de Napoléon, les peintures sur bois de Raphaël (le Saisissement de Sicile, la Vierge au Poisson et la Visitation) étaient en très mauvais état, rongées par la vrillette. Quand elles y furent exposées, la direction du musée du Louvre décida de les restaurer, après avoir consulté des artistes et chimistes de renom. Le restaurateur du musée, Bonnemaïson, transféra sur toile les trois peintures en question.

En ce qui concerne l'opération, certains historiens affirment que Bonnemaïson ne fit que restaurer les trois peintures sur bois et

en attribuent le transfert à Haequin, célèbre restaurateur, qui en collaboration avec Picault, fut le véritable inventeur du rentoilage et du doublage.

D'après le témoignage du peintre Juan Antonio Ribera, qui avait copié le Saisissement de Sicile avant sa sortie d'Espagne, quand cette oeuvre fut rendue en 1819, elle avait perdu son cachet original, ayant pris un ton rougeâtre qu'elle n'avait pas avant. Peut-être ce défaut est-il dû au nettoyage et à la restauration, car le transfert n'altère pas les couleurs.

Les premiers traités que nous ayons en Espagne sur la restauration furent publiés dans la deuxième moitié du XIX^e siècle. Au nombre de ceux-ci, on peut relever "El Arte de la Restauración", édité en 1855 et écrit par Vicente Poleró y Toledo (1), restaurateur de l'ancien musée royal de peintures et de sculptures de S.M.E., ainsi que l'oeuvre de Mariano de la Roca y Delgado, "Tratado de la Limpieza, Forración y Restauración de las Pinturas al Oleo" (2), éditée à Madrid en 1872.

Ces traités se basent sur les ouvrages d'Antonio Palomino (3), du comte de Caylus (4), de Piles (5) et de Mansion (6).

Roca y Delgado nous parle, dans son traité, du restaurateur Nicolas Gato de Lerma qui, en 1864, fut nommé premier restaurateur de la cour d'Isabelle II.

(1) Réédité par Arturo Diaz Martos dans la revue "Informes y Trabajos del Instituto de Conservación y Restauración", n° 12, pp. 101-136.

(2) Réédité par Arturo Diaz Martos dans la revue "Informes y Trabajos del Instituto de Conservación y Restauración", n° 12, pp. 137-144.

(3) A. Palomino, "Museo Pictórico y escala óptica", Madrid, 1715 et 1724.

(4) A.C.P., Comte de Caylus, "Du genre et de l'espèce des peintures anciennes", Mémoire de l'Académie des Inscriptions, volume XII, Paris, 1771.

(5) Roger de Piles, "Les premiers éléments de peinture pratique", Amsterdam, Leipzig, Paris, 1776.

(6) Mansion, "Lettres sur la miniature", Paris, 1823.

Ces traités sont fondamentaux pour la connaissance des méthodes et des matières utilisées en Espagne au milieu du siècle dernier. Poleró se réfère à Juan Garcia de Miranda, cité plus haut, qu'il considère comme le pionnier de la restauration, ce qui prouve les progrès que cette technique avait enregistrés dans la seconde moitié du XIXe siècle. D'après lui, c'est au début du siècle que sont introduits en Espagne l'emploi du vernis comme agglutinant et les techniques de doublage et de stucage.

Ces traités nous expliquent en détail la technique du doublage des toiles, l'application de stucs sur les parties manquantes et la préparation des couleurs de retouche avec des pigments et des vernis, essentiellement à base de mastic. L'adhésif utilisé pour doubler les toiles était fait de pâte de farine ou de colle de pâte, se composant de farine de blé, de colle de menuisier, de jus d'ails (employé comme siccatif), de miel et de térébenthine (térébenthine de Venise).

La technique opératoire du doublage comprend les métiers, équivalant aux faux-châssis, employés par les restaurateurs français au XVIIIe siècle, qui permettaient d'agir sur les deux faces du tableau. A propos du nettoyage, les auteurs mettent continuellement en garde contre l'emploi des solvants "pour éviter que les teintes soient emportées, de même que pour ne pas ôter complètement la patine déposée par le temps... car le nettoyage d'un tableau peut entraîner sa conservation ou sa dégradation".

Les premières normes de restauration des oeuvres d'arts fixées par l'Etat et basées sur des critères actuels remontent à 1901. Elles figurent dans un décret royal sur les restaurateurs des musées archéologiques. En 1904, est constitué le comité de conservation et de restauration des peintures de l'art ancien, auquel on doit la conservation d'un ensemble très important d'oeuvres appartenant au patrimoine artistique national, à l'Eglise et à des particuliers.

En 1920, le musée du Prado est remanié afin de "conserver, avec toutes les garanties de sécurité, notre belle pinacothèque regardée à juste titre par les Espagnols et les étrangers comme l'un des plus riches trésors artistiques du monde". Le musée du Prado avait été créé en 1870 par la fusion des musées de peinture et de sculpture et du "museo de la Trinidad"; le premier abritait les oeuvres picturales provenant du patrimoine royal et le second les objets d'art rassemblés après la suppression des couvents de Madrid, Tolède, Avila et Ségovie.

A l'occasion de cette restructuration du musée en 1920, une importance particulière est accordée à la restauration et à la conservation des oeuvres qu'il renferme. Sont créés les postes de restaurateurs en doublage, de restaurateurs adjoints, de restaurateurs

doreurs et d'assistants des ateliers de restauration de peintures, dépendant tous du sous-directeur à la conservation des peintures et du conservateur restaurateur des sculptures.

En 1942, les quatre Ecoles nationales des Beaux-Arts sont réorganisées (à Madrid, Valence, Barcelone et Séville). On crée la section de restauration des tableaux et des peintures sur bois au sein de la section de peinture, et le cours de restauration des statues au sein de la section de sculpture, matière très intéressante vu la variété des problèmes que pose la restauration des sculptures en bois polychromé, si caractéristiques de l'art espagnol.

Toute cette série de mesures prises dans la première moitié du XXe siècle aboutit, en 1961, à la création de l'Institut central de Conservation et de Restauration des oeuvres d'art, d'archéologie et d'ethnologie. Cet institut se base sur l'expérience accumulée au fil des ans par les deux instituts de Rome et de Bruxelles, surtout de ce dernier dont le directeur, le docteur Paul Coremans, a été désigné par l'UNESCO comme expert conseiller du centre de Madrid.

L'année 1965 voit la fondation de l'Ecole des Restaurateurs avec les sections de sculpture et d'archéologie. L'enseignement est dispensé par des scientifiques et des techniciens de l'institut mentionné ci-dessus. Les matières enseignées sont pour la section de peinture: histoire générale de l'art et de la peinture espagnols; techniques picturales; techniques de restauration; physique et chimie générales appliquées; photographie; muséologie; critères de conservation et de restauration; cours pratiques. Pour l'archéologie: préhistoire et archéologie générales et de la péninsule; dessin archéologique; techniques de restauration du matériel siliceux et organique et des métaux; physique et chimie générales et appliquées; photographie; muséologie; critères de conservation et de restauration; cours pratiques.

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Une autre grande facette de la restauration est celle qui concerne le précieux trésor bibliographique et documentaire espagnol.

En Espagne, au cours du moyen âge, les bibliothèques naissent et se développent à l'abri des monastères et des cathédrales. Il ne fait pas de doute que dans ces centres, il existait le souci de sauvegarder et de préserver les livres et les documents. Ce zèle se manifeste dans les traces de restauration que nous trouvons dans les manuscrits en parchemin aux greffes réalisées sans l'adresse voulue, dans les marges et dans le pli du feuillet, qui nous laissent

voir la main des artistes médiévaux. A cause des défauts de technique, les bords des greffes cachent parfois des lettres et des bouts de texte; l'excès de colle a endommagé le manuscrit et des morceaux de papier ont été appliqués sur les trous du parchemin.

Peut-être l'une des premières tentatives médiévales, dont nous ayons connaissance, visant à conserver des textes et à les protéger des annotations et des possibles outrages du temps, est-elle celle de l'Infant Juan Manuel qui, dans la deuxième moitié du XIVe siècle, fit recopier ses œuvres sur un manuscrit, qu'il corrigea personnellement et que, pour sa conservation, il déposa au monastère de Peñañiel.

A la suite de la pacification de l'Espagne avec la conquête de Grenade, le goût des livres se répandit chez les souverains, les nobles et les ecclésiastiques qui, au moyen d'influences et d'argent, se hâtèrent de se procurer tous les livres dont ils avaient besoin pour la renaissance de la culture en Espagne. En cette période d'humanisme, le commerce florissant des livres et surtout la valeur philologique reconnue aux textes anciens contribuèrent à donner un nouvel élan à l'art de la restauration. Les anciens manuscrits qui passèrent par les mains des humanistes et des libraires et furent conservés dans les grandes bibliothèques fondées à la fin du XVe siècle, présentent les traces des restaurations artistiques des reliures et des matières scripturales. Nous y trouvons quelques initiales refaites, des miniatures retouchées, de nouvelles inscriptions sur des ratures, des interpolations dans le texte, etc.

Au milieu du XVIe siècle, Philippe II créa une très riche bibliothèque à l'Escorial, où il réunit une énorme quantité de livres sur toutes les sciences de l'époque. Une partie de ces livres furent restaurés et placés sur des étagères fabriquées exprès dans ce but, selon les normes de conservation d'alors.

Pendant le règne de Philippe II, les premières règles visant à la perfection en calligraphie furent fixées. Une importante école de calligraphes vit le jour. Leur intervention dans l'histoire de la remise en état des livres et des documents a été remarquée, car ils étaient experts à imiter les lettres utilisées aux époques antérieures.

Cependant, au cours de cette première période et également par la suite, jusqu'à la première moitié du XVIIIe siècle, la technique de la restauration resta dans une phase que nous pourrions qualifier d'expérimentale. Les recettes que donnent les miniaturistes et les relieurs pour nettoyer le papier, raviver les encres et employer les laques et les vernis (qui, avec le temps, ont fini par couvrir l'écriture) laissent fréquemment dans les codex les traces indélébiles des dégâts produits.

Au XVIII^e siècle, siècle par excellence de l'érudition, les bibliothèques privées connurent un grand essor. De même que dans d'autres branches de la restauration, les problèmes de la remise en état des matières scripturales sont brusquement mis en évidence à la fin de ce siècle, à la suite de la découverte des papyrus d'Herculanium (1753). Les recherches furent d'abord menées en France vers 1790 par le Français Chaptal qui procéda à une série de nettoyages de gravures. Ces essais furent suivis en 1797 par ceux de l'Italien Fabrioli. Au tout début du XIX^e siècle, le même Fabrioli élaborait quelques règles pour la lutte contre les insectes qui rongeaient les étagères en bois des bibliothèques, ainsi que pour les greffes de parchemin et de papier.

Toutes ces idées pénètrent de France en Espagne. Dans l'Espagne d'Alphonse XII, très influencée par la France, la bourgeoisie prend une grande importance. Mue par le désir de se cultiver, elle apprécie fort les livres dont elle veut assurer la conservation.

Les premières nominations et les premières normes officielles que nous ayons en Espagne en matière de restauration et de conservation des livres et des documents remontent au commencement du XX^e siècle. En 1915, le poste de restaurateur est créé aux Archives historiques nationales. En 1919, le directeur des Archives historiques demande au directeur général des Beaux-Arts que soit désigné un restaurateur adjoint ayant pour mission de déplier et de relier une énorme quantité de parchemins, "seule façon d'en éviter la détérioration et la perte". En 1940, un concours de recrutement est organisé pour un poste de restaurateur de livres anciens aux Archives historiques nationales. Ce concours se composait d'un examen théorique sur l'histoire de la reliure et sur ses techniques de restauration, et un exercice pratique consistant à restaurer des livres et des documents en papier et en parchemin.

La même année, un laboratoire de restauration de livres est installé dans la Bibliothèque de Catalogne (Barcelone). En 1942, les candidats au poste de restaurateur des Archives générales de Simancas sont convoqués à un concours de recrutement. A la même époque également, on crée à la Bibliothèque nationale de Madrid un poste de restaurateur de livres et de documents.

En 1950, sur l'invitation du Conseil supérieur des recherches scientifiques, le professeur Alfonso Gallo vient en Espagne pour donner des conférences sur la restauration des documents. Il est chargé de mener à bien un projet de création d'un centre similaire à l'Institut de Pathologie du Livre de Rome, dont il serait aussi le directeur, mais ce projet ne se réalise pas.

Pour l'année académique 1956-1957, la Direction générale des Archives et des Bibliothèques sollicite de l'UNESCO deux bourses pour des auxiliaires administratifs qui suivront les cours théorico-pratiques de l'Institut de Pathologie du Livre de Rome. A leur retour, ces boursiers donneront eux-mêmes des cours théorico-pratiques sur la restauration des livres et des documents, pendant trois années consécutives, à l'Ecole de formation des archivistes et des bibliothécaires de Madrid.

En 1961, lors de la fondation de l'Institut central de Conservation et de Restauration des œuvres d'art, d'archéologie et d'ethnologie, il y est créé un département de restauration des gravures, livres, dessins et manuscrits.

Toutes ces tentatives enregistrées à travers l'histoire pour conserver le grand patrimoine bibliographique et documentaire du pays se concrétisèrent lors de la création, en 1969, du Service national de Restauration des Livres et des Documents, sous la dépendance de la Direction générale des Archives et des Bibliothèques. Ce Service a pour mission la restauration de toutes les pièces détériorées appartenant au patrimoine bibliographique et documentaire de la nation, l'étude scientifique des causes de leurs altérations et de la façon de les éviter, ainsi que la formation de techniciens spécialisés.

En 1972, il est adopté une loi pour la défense du trésor documentaire et bibliographique du pays. Elle a pour base la loi de défense du patrimoine artistique national passée en 1933, qui prévoyait qu'une loi spéciale réglementerait la conservation de la richesse bibliographique et documentaire de l'Espagne.

En 1974, le Service national de Restauration des Livres et des Documents a commencé à organiser des cours de formation de techniciens restaurateurs de documents graphiques. Ces cours ont deux buts: former des techniciens restaurateurs afin que le centre dispose d'un personnel convenablement préparé pour pourvoir des postes en son sein ou dans des centres qui dépendent du Service, et faire connaître les énormes problèmes que pose la conservation du patrimoine bibliographique national. La formation dure trois ans et comporte des cours théorico-pratiques sur les techniques de restauration et de conservation du matériel des archives et des bibliothèques, les notions de physique, chimie et biologie appliquées, le processus de restauration des documents graphiques, etc. ainsi que des spécialisations en gravures et dessins, manuscrits et imprimés, et reliure.

L'histoire de la restauration et de la conservation des oeuvres d'art en Espagne est un sujet à peine étudié.

Le thème est très vaste puisqu'il comprend l'architecture, l'archéologie, la peinture, la sculpture, les documents bibliographiques, etc.

Les premières traces de restauration se trouvent dans le domaine de l'architecture, mais ce n'est qu'à la moitié du XIXe siècle qu'apparaissent les premières normes modernes, et au XXe siècle les premières dispositions légales relatives à la conservation et à la restauration des monuments.

En peinture, l'histoire de la restauration en Espagne peut être divisée en quatre étapes:

- 1) Epoque de la restauration empirique
- 2) Incendie du palais royal et première prise de conscience des problèmes de restauration (2e moitié du XVIIIe s.)
- 3) Premiers traités de restauration (2e moitié du XIXe s.)
- 4) Normes de restauration établies par l'Etat (XXe s.).

La troisième grande facette de la restauration est celle qui concerne le monde des livres et des documents. Même si les problèmes en sont latents à travers toute l'histoire d'Espagne, les premières dispositions légales ne font leur apparition qu'au XXe s. avec la nomination de restaurateurs dans les différentes archives et la création en 1969 du Service national de Restauration des Livres et des Documents.

THE HISTORY OF 'DENKMALPFLEGE' FROM THE MIDDLE AGES TILL
ABOUT 1800

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The term of 'Denkmalpflege' originates from the 19th century; the actions characterized by this, which were to preserve and to restore historical monuments, reach far back to history.

The demolition of pagan buildings by the early Christianity led to imperial decrees for the protection of the temples.

These laws, which are transmitted to posterity in the Codex Theodosianus and the Codex Justinianus, prohibited the demolition of the temples, regulated the taking over of spoils and the safeguard of the architectural substance. Theoderich the Great assumed and modified these laws while he consciously entered the antique tradition as an usurper: he tried to legitimate his political claim by preserving the historical monuments in Rome and Ravenna. During the development of this representative act which was according to the political programme, the spoils often received the value of a monument: the dignity and the importance of the old building were transferred to a new construction by taking over details (columns, capitals and so on) and thus received a higher representative value.

So Theoderich the Great took over spoils from Constantinople, Charlemagne from Rome and Ravenna, and Otto the Great and Frederic II from Ravenna - at least one maintains that they originate from there.

These spoils affairs received again a higher ethical value by the scholasticism and dominated the whole high Middle Ages: columns, portals, tympana and sculptures were transferred from the preceding building to the new construction even where it contradicted the new Gothic style.

Towers (Naumburg, Xanten) stilistically had regard for the old architectural substance; crumbled vaults were restored in the 14th century in 'Romanic' style (Basel), destroyed churches were rebuilt referring to the old forms (Lassay/France).

Ruinous stones on the great cathedrals and minsters were

tion of monuments in Europe. Analogically the activity of painting-restorers like: Józef Cholewicz, Ludwik Lepkowski, Wojciech Eliasz and others had nothing to distinguish from the works made abroad. In sixties in the columns of the press take place polemics on the subject of methods for the renovation of paintings.

In the second half of the 19th century in the books by Wladyslaw Luszczykiewicz as well as in many articles by various authors can be found the whole documentation for the then conceptions and we realize that any news in the field of restoration were not strange to polish restorers (for instance the problem of varnish-regeneration etc.). In 1860-1900 many works in the way of wall painting's restoration were carried through. It would surely be interesting to investigate the methods used by these works.

In 1900-18 can be observed how the opinions by J. Ruskin, A. Riegl and M. Dvorak on the preservation of monuments were accepted and adapted in Poland and what was the influence upon the restoration of paintings. The period was very rich in utterances inserted in newspapers, daily and monthly periodicals. Many particulars derive from edited in 1912 'The Diary of I Meeting of Lovers of Native Monuments in Cracov in 1911'. The theory is accompanied by the practical activity in the way of restoration of wall- and easel-paintings. In that time many paintings were discovered and then renovated. During the first world-war between 1914-18 also in the way of restoration of paintings many difficulties have turned up. When Poland in 1918 has become independent arose the problem of rebuilding of industry: agriculture, school-system as well as restoration of monuments.

INFORMATION SUR LES PROBLEMES DE LA CONSERVATION ET DE LA RESTAURATION DES MONUMENTS D'ART DANS LA PRESSE

SOVIETIQUE APRES LA GUERRE

les thèses du rapport

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On trouve des renseignements sur les problèmes de la conservation des collections d'art et les questions particulières de la restauration dans les revues russes à partir du début du XIXe siècle. Commenant au milieu du siècle passé les revues artistiques et les recueils archéologiques, publiés par les différentes sociétés scientifiques, les traitent systématiquement. Avant la Révolution d'Octobre cependant, les revues spécialisées concernant les problèmes de la conservation de musée et de la restauration étaient absentes.

Après la Révolution Socialiste d'Octobre, dans les premières décennies du pouvoir soviétique, c'est-à-dire depuis 1917 jusqu'à la Grande guerre de 1941-45, un réseau de musées d'état et d'institutions s'occupant de la restauration des oeuvres d'art et des monuments de culture a été créé. A la suite de cela, à côté des travaux publiés dans les périodiques scientifiques et dans la presse, les premières éditions consacrées aux problèmes de la restauration et de la conservation de musée ont apparu: Les recueils des Ateliers Centraux d'Etat (aujourd'hui les Ateliers Centraux d'Etat de Recherche de la Restauration d'art de R.S.F.S.R. Grabar I.E. - GCHNRM), 'Voprosy Restavratsii' ('Problèmes de la restauration') et la revue 'Mousainoe Delo' ('l'Oeuvre de musée') (plus tard 'Sovetski Mousei').

Après la deuxième guerre mondiale a commencé l'étape nouvelle de l'histoire de la restauration et celle des publications sur les problèmes de la conservation de musée et de la restauration dans l'U.R.S.S., quand un système de l'organisation de la conservation et de la restauration des monuments de culture et d'art a été revu et on a prêté plus en plus l'attention aux travaux de restauration. Aux sections de la restauration déjà existantes du Musée de l'Ermitage, du Musée d'Etat d'Histoire et de certains autres musées parmi les plus grands, on a ajouté des sections de restauration, créées dans de nombreux musées, bibliothèques et institutions divers; des ateliers spécialisés de conservation ont été organisés dans

un nombre de villes. En 1958 fut créé le centre national des recherches sur les problèmes de la conservation et de la restauration et d'étude des oeuvres d'art: le Laboratoire Central d'Etat des Recherches de la Conservation et de la Restauration des biens de musée d'art (VCNILKR); on forme actuellement un réseau de laboratoires et d'ateliers de conservation à l'échelle nationale dans toutes les Républiques soviétiques ainsi que dans les groupes régionaux.

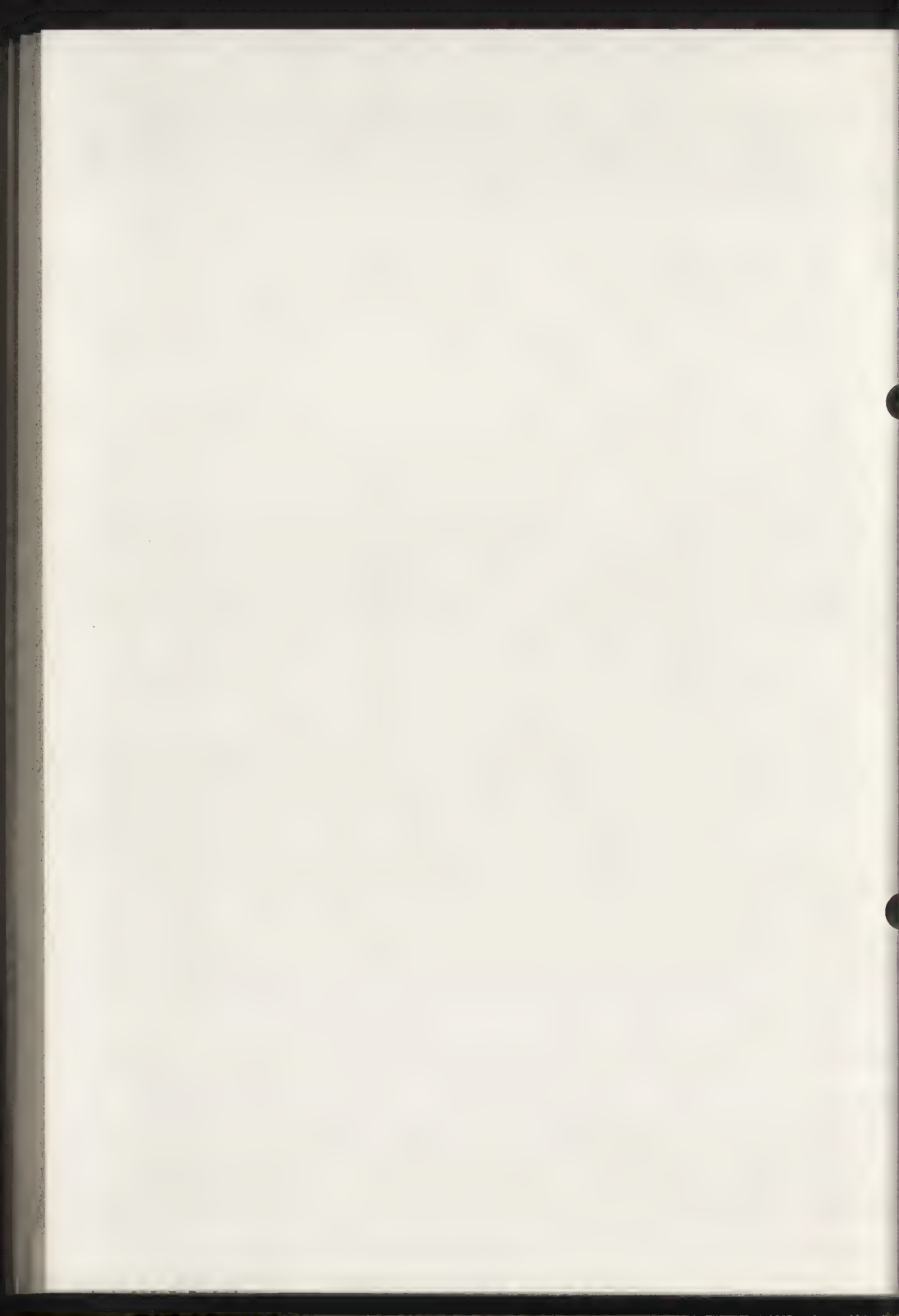
Une grande attention qu'on prête à la conservation et à la restauration des oeuvres de culture et d'art, accroissement du nombre d'institutions de restauration et de sections dans les musées, bibliothèques et d'autres organismes - tout cela a amené une augmentation considérable des publications concernant les questions de la conservation et de la restauration des oeuvres d'art dans l'U.R.S.S. ainsi que le changement de son caractère. La section de l'information scientifique, créée au sein du VCNILKR en 1960 a procédé à l'édition systématique des recueils d'articles sur la conservation, la restauration et l'étude des oeuvres d'art: 'Soobchtchenija' du VCNILKR (avant 1973 les 28 volumes étaient publiés) ainsi que les matériaux des Conférences d'Etat et des instructions différentes; depuis 1973 on a commencé à publier les recueils d'information des exposés des rapports (en 1973 - quatre recueils ont été imprimés; en 1974 - en seront publiés six). Toutes ces publications du VCNILKR ne sont pas limitées au département: au contraire, les restaurateurs et les experts du pays entier y participent. Les recueils spéciaux, publiés par d'autres institutions, ont le même caractère.

Les articles et notes sur la conservation et la restauration sont publiés de même dans les 'Soobchtchenija' du Musée de l'Ermitage, du Musée des Beaux-Arts Pouchkine, du Musée Russe, dans les éditions des Sociétés républicaines de la conservation des monuments de culture: 'Dro 'Drousia Coultoury' (Les Amies de la Culture'; ville Tbilissi, République Socialiste Soviétique de Géorgie) et 'Pamiatniki Tourkmenistana' ('les Monuments de Tourkmenistan'; ville Achkhabad), dans les revues de l'Académie des Sciences de l'U.R.S.S. et des Républiques Soviétiques et dans les autres publications.

Les articles et l'information concernant les institutions de restauration, les restaurateurs et leurs travaux sont souvent publiés dans les revues scientifiques qui sont à la portée de tout le monde, dans les revues littéraires et sociales et dans celles destinées à la jeunesse, de même que dans les journaux centraux, républicains, régionaux et municipaux.

Les bibliographies annotées de tous ces travaux sont pu-

bliées de façon systématique par la section de l'information scientifique de VCNILKR (livraison la plus récente englobant les publications à partir de 1972, paraîtra début 1974).



THE DEVELOPMENT OF THE CZECHOSLOVAK RESTORATION SCHOOL
IN THE YEARS 1945 - 1965

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The year of the liberation of our country from the fascistic occupation by the Red Army is an important point - similarly as in other disciplines - also in the development of the Czechoslovak art of restoration. In a short time after the war there were in the reopened National Gallery exposed two pictures, The Holy Virgin of Roudnice and The Holy Virgin of Zbraslav, with an extensive documentation of the process of restoration. Both has restored Bohuslav Slánský. It is nearly evident that this exposition made for the first time the public acquainted with modern principles of restoring.

A year later /1946/ B. Slánský became professor on the Academy of the Fine Arts for the new discipline of painting and conservation technics. Shortly afterwards was founded the same discipline in Bratislava, on the High School of Arts, where was appointed as professor a collaborator of B. Slánský from the National Gallery, Karel Veselý.

It is worth to be mentioned that the foundation of a restoration school in Prague and in Bratislava has formed the primacy of Czechoslovakia, because till this time nowhere world a high school discipline of restoration was formed.

During the years increased the number of graduates as painters and sculptors with a specialization

as restorers, and they became members of the Federation of the Fine Arts. Here, in the Federation, an independent branch of restorers, painters and sculptors was formed. At first it was necessary to overwhelm certain difficulties with the aim of defending the equivalence of the restorers with other artists. It was necessary to prove, that the restoration is an art and not a sheer handicraft, a discipline joining in it more factors, the art being the most important of them. The restorers must have a high artistic feeling, must know some scientific disciplines and at the same be skilled. Owing to the understanding of the leading of the Federation became at last the restoration equivalent discipline to the disciplines of painting, sculpting and graphic art.

Nearly in the same time it was necessary to secure also the economic view of this art. As a part of the economic organization of the Federation, the Fund of Fine Arts, it was formed also a Restorers Committee. These Organization problems occupied the author of this paper, who was secretary of the Restorers Committee in the years 1952 - 1962.

Besides the problems of organization and economics of the restoration in the years after the war there were also solved the fundamental problems of the restorers work. One of these problems was also the controversy about the esthetics and technics of retouching. There existed still in this time a merely strong group of the so called church painters, who persisted on the opinions of the 19th century. The aim of their activity was to preserve the sujet and the authenticity of the work of conservation of

its remainders was no problem at all. The picture was "refreshed" and mostly were great parties senseless repainted.

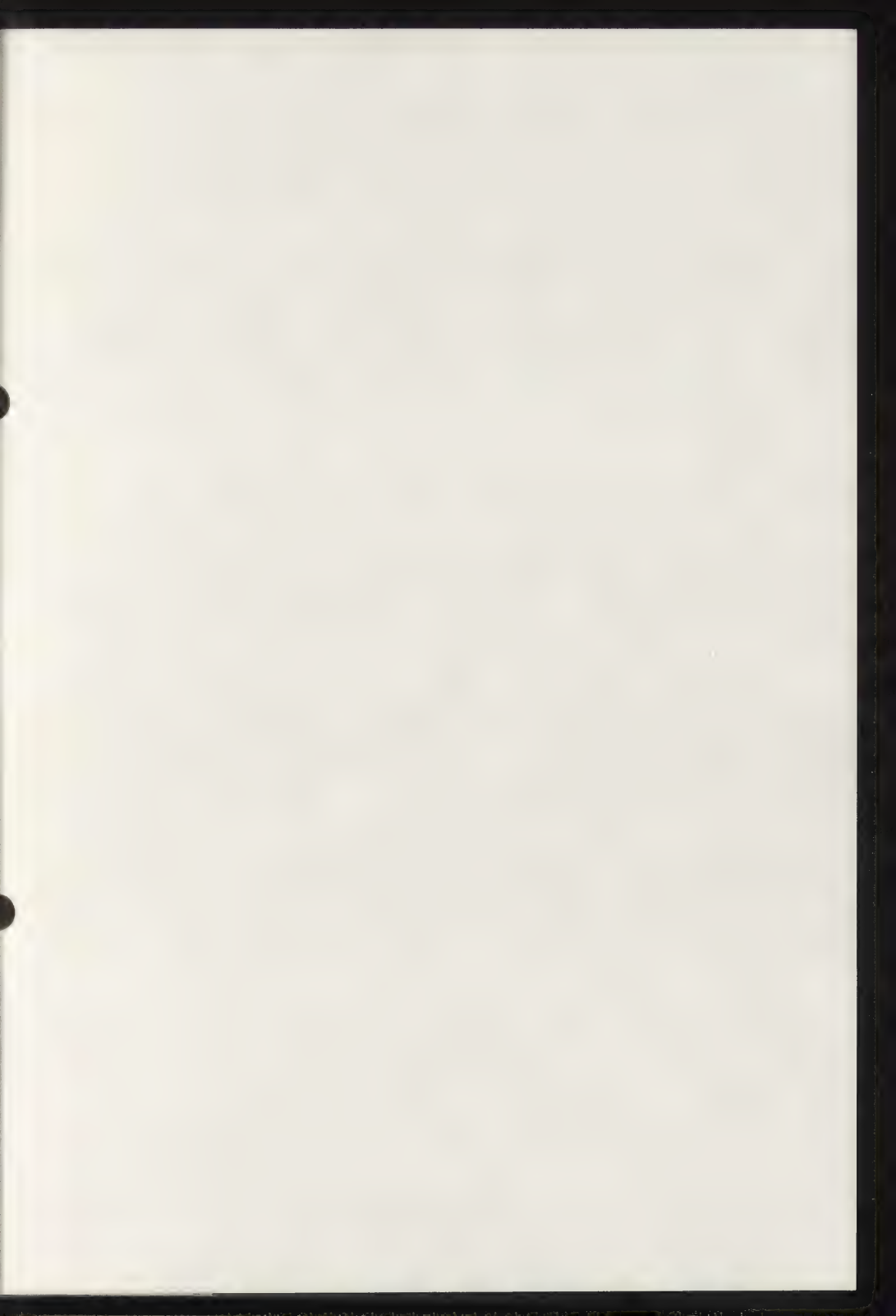
The controversy between these "romantics" and modern restorers culminated by occasion of restoring the mural pictures originating from the last quarter of the 14th century in the church of St. Apollinaire in Prague. These painting were restored by the pupils of professor Slánský and under his personal leading. The fundamental question was to make a retouch, which can easily be removed and which represents a neutral tone in the missing parties of the picture. The matter of the controversy were the missing parties of the faces, hammered out in the times of iconoclasm. The refusal of repainting the missing parties was origin of polemics in the review Památková péče between the restorer František Petr and professor B. Slánský. Prof. Pešina in the catalogue of the Slánský exposition in the year 1972 writes that "professor Slánský demonstrated his high superiority both artistic and moral and gained his victory. He pleaded not only for himself but also for the school the representant of which he was and the school was in the polemics firmly on his side."

From the beginning of the sixtieth years - during mere fifteen years of its existence- the czechoslovak school of restoration became well known and belongs to the worlds best. In this time the restorers grouped around their teachers, prof. Slánský and prof. Veselý, feel also a necessity of making the public acquainted with their work. In 1964 was formed a restorer group R - 64 uniting mostly the graduates and teachers of both high schools and members

of the restoration atelier of the National Gallery. A year later made this group an exhibition, one of the first restorers exhibitions, in the Kramář Gallery in Prague.

It is significant that this exhibition was made in a gallery bearing the name of the director of the National Gallery of the pre-war time, Dr. Vincenc Kramář, who with prof. Slánský gave the first impulse and aim for the new conception of restoring. The exhibition demonstrated the principles, ways and possibilities of restoring works of art, paintings on canvas and wood, polychromied plastics, mural paintings, included their transferring, restoration of gobelins and graphics. The exposed objects were accompanied by an extensive documentation.

The public and the experts could see in this exposition a clear program of solving the problems of modern restoration.



SOME THOUGHTS ON AESTHETIC ASPECTS OF PICTURE CLEANING

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Papers read at recent I.I.C. conferences indicate that methods of scientific investigation as preparation for the treatment of oil paintings are increased and improved. Finer and more delicate discrimination can be applied in observation and in practice. As this is the case in regard to the physical facts of the picture it can perhaps be safely assumed it will also be that in regard to aesthetic aspects of the picture. Certain facts can, of course, be established by investigation into what is historically known of the picture and certain aspects of style can be factually determined; and even aesthetic elements such as typical use of line, tone, colour, can be, often, fairly objectively ascertained: however it is credible that the emotional content of the work is far more difficult, if not impossible, to assess. Nevertheless it remains imperative that it be assessed because it is, as we all realize, the *raison d'être* of the work of art and the central cause to which all other aspects - colour, radiance, tone, shadow, surface encrustation, etc. - are contributive and to which, of course, they owe their being.

The aspect I speak of is the actual emotional impact of the painting as distinct from its formal or its intellectual aspect. I speak of this, if I may, as if it can indeed be separated from that with which, as in all creative work, it is so inextricably mingled, one aspect giving reason and existence to the other. However as one may discuss formal aspects of a painting and intellectual aspects one may perhaps also discuss the emotional aspect. This aspect is difficult to define and perhaps it is best to use the words of great and acknowledged criticism.

The following passage is from Sir Kenneth Clark's introduction to *Masterpieces of Fifty Centuries*,¹ an exhibition held at the Metropolitan Museum of Art, New York.

"So when form moves us most, the idea has been warmed by a feeling of our normal human needs. And next to survival, the strongest of these needs is the sexual impulse. A narrowly sexual aesthetic is incomplete, but it seems probable that our feelings of intense satisfaction when we contemplate certain pieces of sculpture or even pottery, our pleasure in apprehensible bulk, in smoothness of transition, in ratios of size between spheres and cylinders, arise from a physical cause rather stronger than the intellectual consolations of geometry. Ruskin said that ultimately sculpture derived its power from 'bosiness or pleasant roundness'. - One may speculate how far he was aware of the implications of this phrase, which the conventions of his time did not allow him to explore."

¹ Sir Kenneth Clark. *Unity in Diversity*. Introduction to *Masterpieces of Fifty Centuries*. The Metropolitan Museum of Art (1st Edition). E.P. Dutton & Co. Inc., New York, in association with the Metropolitan Museum of Art, 1970, p. 15.

The lines refer to an unusual but common quality of great art. Sir Kenneth Clark is speaking specifically of sculpture, but nevertheless the sensation he describes is one many people are familiar with in their experience of great art - a sense of deep pleasure given by experiencing the third dimension and its attendant associations. We might refer in this context especially to the painting of the western world from, say, the late Middle Ages to the modern classics. Not all works of art have this quality, but most great ones do.

Bernard Berenson¹ refers to physical response as part of the enjoyment of great art.

"Space-composition is much more potent. Producing as it does immediate effects - how and why cannot here be discussed - on the vaso-motor system, with every change of space we suffer on the instant a change in our circulation and our breathing - a change which we become aware of as a feeling of heightened or lowered vitality. The direct effect, then, of space-composition is not only almost as powerful as that of music, but it is brought about in much the same way; for, although many other factors enter in to produce the impression made by music, the body of its force grows out of the revolutions it produces in the vaso-motor system. Hence the likeness so often felt, but, to my knowledge at least, never explained, between music and architecture - the latter, in so far as it is not merely superior carpentry, being essentially a manifestation, the most specific and the most powerful, of the art of space composition."

Although Berenson is not describing precisely the type of "bosiness" or roundness that Sir Kenneth Clark refers to he nevertheless is giving an idea of the beholder's pleasure in participating in remembered physical apprehensions of the three-dimensional in space that he senses he must have in common with the artist because he, the beholder, sees them powerfully evoked in the painting.

In the introduction² to *Masterpieces of Fifty Centuries*, Sir Kenneth Clark says of Cézanne,

"Few painters have had a nobler sense of form in the simple terms that I described earlier; but he determined to give form an even fuller development (and plénitude) by rendering it with the maximum strength of colour. The simpler his subjects, the more profound his effects; and no doubt the effect on our emotions of his pears and apples is due to very deep analogies in human experience."

¹ Bernard Berenson, *Italian Painters of the Renaissance*, Volume Two. Phaidon. London and New York, Paperback Edition, 1968, p. 88

² Op. cit., p. 19.

The words suggest Cézanne's acute awareness of "business" or depth giving vitality or a sense of heightened intensity of life to the picture. Leonardo da Vinci¹ refers to relief as being "the importance and soul of painting".

We may take it that the element of "business" has been found by great artists and critics to be something peculiar to great art. It conveys a specific type of emotion in its creation of volume and in its contribution to the total form and impact of the composition. The effect such roundness or development of volume and depth gives to a picture is expressed in a paragraph by, again, Sir Kenneth Clark.²

"TITIAN

The Entombment

From far away the assault on my emotions is immediate and commanding, like one of the great first lines of Milton - 'Of Man's first disobedience' or 'Avenge, oh Lord, Thy slaughter'd saints' - and in this state of heightened feeling I cannot distinguish, any more than Titian could, between the drama of the subject and the drama of light and shade. His root idea was concerned equally with both. It was that the pale body of Christ, borne on a white sheet, should hang in a pool of darkness, as if from a human cave; and that beyond the cave should be two buttresses of vibrating colour."

It is clear that the darkness in the composition contributes enormously to the emotional force of the picture and to the scope of possible physical enjoyment of sensations of plasticity that the picture gives rise to.

"Business" of detail consists, of course, in the creation of the volume of particular objects in the picture and this is achieved by giving an impression of the shadow that we are aware imparts the aspect of third dimension in actual life. It can be imagined that it is the essential moving part of art, as Leonardo says, its "soul and importance". The creation of "business" in a painting contributes to the emotive power of the particular object and the combined effect of "business" absorbed into the total surface and spatial effects of the composition greatly increases the composition's emotional power.

Certain paintings, of course, rely more on "business" or emotionally expressed three dimensional aspects than others. When such "business" or shadowiness is removed the painting loses its impact. The response to "business" is, in fact, a physical response

¹ The Notebooks of Leonardo da Vinci, Volume II. Arranged, rendered into English and Introduced by Edward McCurdy. Reprint Society, London 1954, p. 216.

² Kenneth Clark, Looking at Pictures. John Murray, 50 Albemarle Street, London, 1960, p. 21.

and though a critic may be aware, when looking at the picture, of many aesthetic qualities he may not always necessarily be aware, as is implied by Sir Kenneth Clark in the passage from the introduction I quoted above, of the quality of emotional impact expressed by the artist in his application of the pigment and in the distribution of compositional masses and of effects of depth and volume. It is difficult to imagine how this emotional aspect of painting can be determined factually depending as it does largely on instinctive and recalled physical apprehensions that may or may not be shared by everyone. In such cases one can only rely on one's instinctive responses backed by the voiced opinions of great critics.

Another manner in which emotion is conveyed in painting is in the application of pigment. Thick pigment as, for example, in the works of Van Gogh, is often used to give vent to strong emotion or, and perhaps frequently, also, to express sensual reactions to objects and their associations as notably in the works of Rubens, Rembrandt, Renoir. Thickness or particular methods of application of pigment, for instance transparent application or rough application, or application in large smooth surfaces or in small broken patches are part of the sensual quality of the picture and can also be an expression of the physical and emotional energy of the artist.

It may be interesting to remember the point that oil painters have not always sought to represent nature as did the Impressionists. An interesting study, The Academy and French Painting by Albert Boime¹, describes the manner in which Pre-Impressionist painters made direct studies from nature that were later turned into works expressing more intellectual - that is, in respects other than those of direct transcription of nature - conceptions in the studio. An aversion to what is 'literary' in painting need not lead to a dislike of what is conceptual in the intellectual or spiritual sense. It may well be that the colour and light of Impressionism were means particularly expressive of an inner world of experience peculiar to artists subject to the social, scientific and situational influences of that period. The particular colour of Impressionism is also a particular phenomenon of France. In some hot countries shadows simply are, at times, black.

The darkness in Romantic paintings may actually have been a means of giving vent to very deep feeling. The following passage is from the classic work on picture cleaning, The Cleaning of Paintings.²

"In seeing at the big Delacroix exhibition in the Louvre a great number of his works well cleaned I wondered how he could ever have believed that he was nearing or attaining Rubens' luminosity unless he never saw a clean Rubens. At any rate he was surrounded by

¹ Albert Boime. The Academy and French Painting. Phaidon, 1970.

² Helmut Ruhemann. The Cleaning of Paintings. Problems and Potentialities. With Bibliography and supplementary material by Joyce Plesters. Faber and Faber, 24 Russell Square, London, 1968, p. 52.

pictures covered with brownish accretions and perhaps, by comparison, his own fresh paintings looked colourful and bright."

The suggestion is that Delacroix may have painted differently had he seen cleaned Rubens. It may well be Delacroix simply wished to express his powerful feelings of delight in the plasticity of objects and did so by using dark shadows. Frequent references in the Journal indicate that Delacroix was very interested in aspects of Rubens' work other than light and colour. Part of the entry in the Journal¹ for October 20, 1853, reads:

"What an adoration I have for painting! The mere memory of certain pictures, even when I don't see them, goes through me with a feeling which stirs my whole being like all those rare and interesting memories that one finds at long intervals in one's life, and especially in the very early years of it."

In the same entry, speaking of Rubens, he says:

"How strange the picture which perhaps gave me the strongest sensation, the Raising of the Cross, is not the one most brilliant through the qualities peculiar to him and in which he is incomparable. It is neither through colour nor through the delicacy nor the frankness of the execution that this picture triumphs over the others, but curiously enough through Italian qualities which, in the work of the Italians, do not delight me to the same degree."

And further on:

"The essential thing about these works is their reaching for the sublime which comes in part from the size of the figures. The same pictures in small dimension would, I am sure, produce quite a different effect on me. In the effect of Rubens and in that of Géricault there is also an indefinable something of the style of Michaelangelo which adds again to the effect produced by the dimension of the figures and which gives them something terrifying."

The last words imply that these three great artists have a quality in common, perhaps grandeur of structure, or grandeur in development of volume on a large scale, though each may achieve this by different means. It is true that Géricault may have made a technically bad choice in using bitumen, but it nevertheless satisfyingly gave outward emotional expression to an inner emotional need. In a footnote in Lorenz Eitner's study Géricault's Raft of the Medusa² the following appears:

¹ The Journal of Eugène Delacroix. Translated from the French by Walter Pach. Crown Publishers, New York, 1948, pp. 334-335.

² Lorenz Eitner. Géricault's Raft of the Medusa. Phaidon Press, 1972, p. 41.

"Clément obtained from Géricault's assistant, Jamar, a list of the colours used by Géricault in the order in which they were arranged on his palette (op. cit. p. 41, Note 2): vermilion, white, Naples yellow, yellow ochre, terre d'Italie (presumably a red ochre) ocre de Brie (presumably a yellow ochre), raw Sienna, light red, burnt Sienna, Crimson lake, Prussian blue, peach, black, ivory black, cassel earth, bitumen (asphaltum)."

Delacroix (entry to the Journal March 5, 1857)¹ wrote in connection with studies of cadavers by Géricault made with such a palette:

"This fragment from Géricault is truly sublime: it proves more than ever that there is no serpent nor odious monster, etc. It is the best argument in favour of the Beautiful as it should be understood."

It is clear Delacroix saw beauty in Géricault's work in Leonardo's sense of the word - relief is "the soul and importance of painting". Géricault, also, clearly wished to express by the darkest darks he could achieve - actually adding bitumen to black - extreme "business" and profound feeling.

Subjective assessment of elements in a picture is of vital importance. The fine achievements of science in the conservation of oil painting can only be bettered with ever increased imaginative co-operation with informed subjective evaluation. It might also be remembered that the world of science itself need not necessarily be seen as fixed, but, as some contemporary philosophy sees it, vacillating or conjectural, consisting of hypotheses and theories that may at any time be refuted and replaced by others, possibly better and more developed.

I feel that in the cleaning of pictures the sensual effects created by application of pigment should be given especial attention. In pictures that are highly evocative sensually the loss of volume or the loss of appearance of fatness in the pigments or vehicle can deprive the picture of essential effects. That this can happen is apparent to the naked eye and has been backed by scientific investigation, as, for example, in the extremely fine publication on varnishes and solvents by R.L. Feller, N. Stolow and E.H. Jones.² A paragraph from the summary of part 4 reads:

"The conclusions drawn from the various studies are important and far-reaching. The cleaning of a virgin oil paint surface (i.e. one never previously in contact with solvent) will lead to action which is irreversible. This may serve to explain the "chalky" condition of some cleaned pictures. While

¹ Op. cit., p. 575.

² Robert L. Feller, Nathan Stolow and Elizabeth H. Jones. On Picture Varnishes and Their Solvents. Revised and enlarged edition. Press of Case Western Reserve University, Cleveland and London, 1971. p.111.

leaching cannot be eliminated entirely, mechanical action upon softened films resulting from swelling can be minimised. | Acetone may be used relatively safely if the contact with the surface is minimised, small quantities are used and adequate time for evaporation is allowed."

The paragraph continues, suggesting various ways by which solvent action can be controlled. Perhaps further investigation in this field may be able to make practical what is both scientifically possible and artistically desirable.

I also feel that the effects of "bosiness" or darkness or shadowiness should be given great attention although I think it is true such effects are not quite in keeping with contemporary taste. Transcription from nature has not always been, if it ever has been, the sole aim of the painter. We know that many painters of the Renaissance sought to create in painting a world of the ideals of Neo-Platonism; that in paintings of the late Renaissance visions would seem to emerge from a world of idyll or inner imagination and reflection. Occurrence of shadowiness in these paintings has, both in the composition and in the creation of volume, a poetic force. Colour and light in the substantial parts of the picture emerge as from a dark matrix, as if from the imagination or from the inner concept of some ideal world. Effects of veiling over the material and substantial reality of the flesh as in Venetian painting give a sense of the combination of the real and ideal, mingled and compared, that played so great a part in the philosophy of the day.

The composition of many of the oil paintings of the period I have referred to would seem formed by a creative act where form, mass, colour, light, shade, line, thinness or thickness of pigment are made to conform by emotion and by physical and spiritual energy to one central concept. The third dimensional depth in a picture is created by darkness or shadowiness. To do this the artist may simply have used black, as Géricault, or he may have used dark colours that give an equivalent of black or that suggest weight or shadow: he may even use degrees in the thicknesses of pigment to achieve this. It is also the practice of many painters to pull one dark, though rich, colour transparently over another, the intensity of colour thinning out at the edges of the shadow area to give an effect of shadow merging into light. The occurrence of this practice does not need scientific investigation as such strokes are apparent to the naked eye in the work of van Dyck, early Augustus John, Renoir, Rubens and many others. It is, in fact, a common painterly practice though, of course, varying powers of conception or degrees of technical skill bring about differing results. Such shadows are formed into part of the linear, mass, spatial and tonal composition of the picture by the creative act. It is not impossible that the compositional force of a picture can be diminished if areas of dark transparency, or areas of shadow suggested in other ways, are altered. It may be possible that improved methods in investigating pigment layers will also enable an even finer distinction in ascertaining differences of inherent pigment and vehicle and external varnish than is at present possible. The difficulties of doing this with sufficiently refined precision for artistic needs up until quite recently have been expressed by

those who are qualified to do so. I quote from the very moderate and finely balanced article by Rees Jones¹ that appeared in the Burlington Magazine in 1962 and must surely always be considered relevantly.

"The opaque method² of examining cross sections through the layers in a painting fails to disclose the very thin surface layers that are vital to the visual appearance of the painting. Failure to take into account the limitations of the analytical methods may lead to oversimplification of the problems involved in cleaning. There is no doubt but that in many paintings the artists' technique and the hand of time result in such uncertainty about the composition and structure it is impossible to define a geometrical boundary between paint and varnish. There will also be anomalies in colour and value due to pigment change, increased transparency of the paint, and so on, which undermines the status of purely physical criteria for determining the end point in the cleaning process.

Footnote 2. This restriction does not apply to transparent cross sections which can be examined at sufficiently high magnifications. See Coremans and Thyssen. Bulletin de l'Institut Royal du Patrimoine Artistique, II (1959) p. 41."

One feels that care and caution should be the handmaids of art and science in regard to the aspects I have mentioned.

¹ S. Rees Jones. Science and the Art of Picture Cleaning. Burlington Magazine, 54 No. 707, 1962, pp. 60-62.

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MATÉRIAUX SUR L'HISTOIRE DE LA RESTAURATION DES
COLLECTIONS DE MUSÉE EN RUSSIE
(AVANT LA RÉVOLUTION D'OCTOBRE)

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L'histoire de la restauration des oeuvres d'art en Russie n'était pas encore écrite. Le présent aperçu où l'auteur fait une tentative de la systématiser, est loin de prétendre à être complet. Il est rédigé sur la base de données d'archives et de publications contenant des renseignements variés et bien fragmentaires.

Quand la conservation et la restauration des oeuvres d'art font-elles leur apparition en Russie? On ne pourrait pas répondre à cette question par un seul mot. En effet, le simple entretien d'une oeuvre, sa "réparation" et manutention dans un état satisfaisant - tout cela présente déjà sa conservation. En ce sens la restauration, et plus précisément la réparation ou le renouvellement, ont pris naissance en même temps que l'art professionnel. Pour les peintures anciennes russes (icônes) - se sont X^e-XI^e siècles, pour les peintures à l'huile de chevalet et pour les peintures murales monumentales - c'est la fin du XVII^e siècle, quand les maîtres de la Salle des Armes, les premiers en Russie, ont commencé à peindre sur la toile (le taffetas).

La conservation et la restauration dans la signification moderne du terme naquirent en Russie plus tard.

Leur début il faut situer, faut d'autres informations, au milieu du XVIII^e siècle, quand la passion de collectionner des oeuvres d'art a battu son plein et les collections étaient considérées en tant que richesse nationale.

Il serait aussi naturel de supposer le temps plus ancien. Au XVII^e siècle par exemple nous rencontrons des recommandations concernant l'entretien des oeuvres d'art, notamment des icônes russes originales. C'étaient les maîtres d'icônes qui ont eu une influence sur les procédés et les méthodes de la restauration des peintures à l'huile de chevalet. Ils connaissaient également mieux que personne la technique de la peinture, les divers matériaux: supports, préparations, couleurs, huiles de lin cuite, liants. Ils possédaient des traités anciens où il y avaient les recettes et les renseignements sur la réparation des icônes anciennes et les conseils, par exemple comment enlever l'huile de lin cuite à l'aide d'ammoniaque, d'alcool vinique, ou encore comment introduire la colle sous une couche de "levkas" (l'enduit) et même comment fabriquer des fausses peintures. Ce n'est certainement pas un hasard que les maîtres d'icônes étaient les meilleurs restaurateurs et pouvaient de même effectuer le traitement des peintures à l'huile.

Dans la deuxième moitié du XVIII^e siècle la Russie voit apparaître les restaurateurs isolés, essentiellement d'origine étrangère, qui malheureusement n'étaient pas souvent les personnes compétentes et ne cherchaient qu'à gagner de l'argent. Ils travaillaient, soit constamment, soit provisoirement, auprès de grandes collections de peintures, d'objets de l'art appliqué, de sculptures; ils pratiquaient aussi la restauration d'une manière privée.

Les noms des premiers restaurateurs, qui nous sont parvenus, se trouvent liés avec le Musée de l'Ermitage. La fondation de l'Ermitage monte à 1764, quand une collection renfermant 225 tableaux des peintres hollandais et flamands, achetée à Berlin sur l'ordre de l'impératrice Catherine II, a été apporté dans le Palais d'Hiver. A cette époque la collection d'Ermitage comptait 2000 tableaux. Certes, une telle collection avait besoin d'une surveillance systématique et qualifiée et de mesures préventives de conservation.

Avant la création de la galerie de peinture Lucas Conrade Pfandtselt, peintre de la cour hollandais, a été invité en qualité de restaurateur-conservateur,

pour assister Grott, maître-conservateur; puis il est devenu, selon les documents, le premier restaurateur de la section de tableaux de l'Ermitage d'empereur. L.C. Pfandtselt a été chargé de réparer, renouveler et conserver en bon état les divers tableaux. On l'appelait l'artiste de la restauration "mécanique". On sait qu'il exécutait des opérations de transposition des peintures du bois sur le cuivre, ainsi que sur une nouvelle toile. Nous avons notamment le tableau de Lucas Cranach II "Le christ et la pécheresse", transposé de panneau sur cuivre et portant au revers la signature du peintre.

En 1780 Martinelli de Venise remplace L.Pfandtselt au poste de conservateur. Martinelli ne s'occupait pas lui-même de la restauration, mais auprès de lui travaillaient les artistes, invités de l'Académie des Beaux-Arts russe. L'Académie chargeait d'habitude ses pensionnaires, envoyés en Italie, en Hollande d'y prendre connaissance de la restauration des peintures.

En 1797 Frants Ivanovitch Labenski fut nommé au poste de conservateur de la galerie; il en était à la tête jusqu'à 1849 et c'était lui qui avait créé à l'Ermitage le premier en Russie atelier de restauration avec une école auprès de lui pour la formation des techniciens. F.I. Labenski, au moment de sa nomination, avait trouvé le métier de restauration dans un état négligé. Il avait invité Peronar, l'étranger, pour qu'il fit les restaurations mécaniques; malheureusement ce dernier "...n'était pas bien versé dans le métier..." et ne s'intéressait pas aux affaires de la galerie. Peronar était chargé d'exécuter le transfert de bois sur toile du tableau de Giorgione "Youdif avec la tête d'Olophérne", attribué à cette époque à Raphaël. Au début du XIX^e siècle jusqu'à 1817 la restauration picturale s'effectuait par Pirolli, peintre.

F.I. Labenski avait fait tout son possible pour former des restaurateurs russes issus du personnel du Palais. En 1801 il avait désigné au poste de restaurateur technique de la galerie Andrej Philippovitch Mitrokhine (1766-1845) qui est devenu le premier restaurateur russe et qui avait travaillé à l'Ermitage pendant plus de 40 ans.

A.Ph. Mitrokhine naquit à Toropets, en province de Pskov, y faisait son apprentissage en peinture, puis il était soldat du régiment de Sophie; en 1792 il fut admis au service du Palais d'Hiver comme laquais, ensuite il était valet de chambre à l'Ermitage. F.I. Labenski appelle Mitrokhine "le meilleur dans son

art... inventeur de la restauration mécanique en Russie", qui avait trouvé "un moyen de la transposition des peintures de bois sur toile et en travaillant sans relâche, l'avait porté à la perfection, prouvée par des nombreuses opérations"... En 1840 Mitrokhine avait généralisé son expérience dans une publication: "Règles de transposition des peintures de bois sur toile". A partir de 1820 Mitrokhine et ses élèves commencent à appliquer au dos des panneaux le parquetage dans le but d'empêcher leur gauchissement. En outre cette transposition où toutes les opérations en effet se trouvaient réunies, Mitrokhine effectuait également recollage des planches de bois, rentoilage, enlèvement des encrassements des tableaux, retension des toiles (sur le nouveau châssis), retouches, vernissage, des peintures.

Le 30 avril 1819 F.I.Labenski, aidé par Mitrokhine et soutenu par le prince A.N.Golitsyne, ministre de l'instruction publique, ainsi que par l'Académie des Beaux-Arts, fonde une école des restaurateurs, la première en Russie, dans laquelle les quatre élèves, étudiants de l'Académie des Beaux-Arts, aient été admis. En 1825 on adopte le statut de l'école, selon lequel un élève n'avait pas le droit de demander sa démission pendant 6 années, après quoi il était élevé au grade de restaurateur-adjoint. Les peintres F.A.Rybina et F.I.Tabountsov étaient les meilleurs élèves et puis - restaurateurs doués de talent; le premier avait travaillé à l'Ermitage jusqu'à 1845, le second - jusqu'à 1861. Les futures techniciens étudiaient simultanément les méthodes de la restauration technique et picturale.

Jusqu'au milieu du XIX^e siècle 4 à 6 restaurateurs ont travaillé dans l'atelier de restauration de l'Ermitage à des périodes différentes. Entre 1816 et 1845, ils ont traité près de 1000 tableaux, appartenant à l'Ermitage, aux palais de banlieues, au Monastère d'Alexandre-Nevski et d'autres. On faisait des traitements des oeuvres d'art uniques avec des soins et des précautions infinies, conformément à des permissions spéciales. Mitrokhine avait exécuté lui-même les restaurations des tableaux des maîtres célèbres, tels que Raphaël, P.Rubens, Salvator Rosa, G.Romano, Reynolds et d'autres.

L'histoire de la restauration des oeuvres d'art à l'Ermitage dans la deuxième moitié du XIX^e - au début du XX^e siècle est liée avec les trois générations des restaurateurs de famille de Sidorovs, travaillées dans ce Musée jusqu'aux années trente du XX^e siècle.

Dès leur arrivée, la transposition des tableaux de panneau sur toile prend une ampleur extraordinaire. Nous avons l'impression qu'on faisait souvent cette opération ne pas pour remédier aux dégâts des oeuvres, mais seulement dans le but de montrer ses technique et habilité. Il faut signaler, que les résultats des transpositions faites par Sidorov sont fréquemment de qualité et de maîtrise inférieures en comparaison avec ceux du travail exécuté par Mitrokhine et ces adjoints. Avant la Révolution d'Octobre à l'Ermitage, à l'exception des Sidorovs, travaillaient les restaurateurs de peinture suivants: D.F.Bogoslovski, S.P.Jaremitch, L.P.Albrekht, I.I.Vasiliev.

A Moscou, également, après la création de la Galerie de Trétiakov en 1854, les problèmes de conservation des oeuvres de peinture réalisées selon les méthodes techniques de restauration commencent à se poser et se résoudre. P.M.Trétiakov, à côté du rassemblement des oeuvres d'art, prêtait une grande attention à la protection des tableaux contre les dégâts; il connaissait la technique de la peinture, les matériaux, le métier de restaurateur et se souciait beaucoup d'une conservation correcte des objets d'art. Il tenait pour principe ne pas toucher au tableau sans avoir mis des gents tricots blancs, contrôlait lui-même les conditions d'humidité et de température, protégeait les peintures contre la lumière du soleil et les impuretés d'atmosphère, ainsi qu'enseignait considérer un tableau comme objet "saint".

Le temps nous avait conservé les noms des premiers conservateurs de musée qui exécutaient aussi fréquemment des traitements préventifs. Citons par exemple le nom de A.O.Moudroguelenko, ancien valet de chambre de P.M.Trétiakov. Une pièce isolée était destinée aux travaux de restauration. Après A.O.Moudroguelenko les traitements des oeuvres d'art appartenant à la Galerie furent effectués par A.M.Ermilov, N.A.Moudroguel, A.G.Dogadine.

Dès la fin du XIX^e siècle A.K.Fedorov était invité à la Galerie pour y exécuter des restaurations techniques. Il est devenu ensuite le premier spécialiste, bien connu comme fondateur de l'atelier de restauration, maître d'un grand nombre de restaurateurs, y compris ses trois fils.

Il convient de remarquer, que la Galerie, du moment de sa fondation, était guidée par des bons connaisseurs en arts. Après la mort de P.M.Trétiakov, le prince V.M.Golitsyne était devenu curateur de la Ga-

lerie, puis, en 1905 I.S.Ostrooukhov, collectionneur et peintre bien connu, le remplace, et de 1913 à 1920 - I.E.Grabar, célèbre historien de l'art, peintre et restaurateur. Ils apportaient tous une grande attention aux problèmes de conservation et présentaient des soins extrêmes aux traitements des oeuvres. C'est pourquoi la collection de la Galerie dans son ensemble s'était trouvée dans un état de conservation satisfaisant. En 1899 on avait installé la fonction de conservateur et en 1906 - on en avait adopté une instruction. Conservateur fut chargé de surveiller aux traitements des oeuvres d'art.

Un nouveau chapitre de l'histoire de la conservation et de la restauration des peintures de Galerie commence à partir de 1913, quand au poste de directeur fut nommé I.E.Grabar, historien de l'art et peintre déjà connu qui est devenu après la Grande Révolution Socialiste d'Octobre le fondateur de l'école soviétique de restauration des biens culturels. On a crée, dans la Galerie, un atelier de restauration, on a procédé à la description des tableaux, on a précisé les problèmes de conservation et la restaurations des peintures, on a fait des photographies, on a étudié les questions d'entretien de l'objet, on a fait vitrer des tableaux et puis on a effectué "mise dans l'enveloppe" - soit on a réalisé la protection du dos du tableau contre les effets de l'air pollué et des brusques changements hydrométriques.

L'évolution de la restauration au Musée Russe l'empereur Alexandre III, inauguré en 1895, était analogue à celle de la Galerie Trétiakov. En 1910 les restaurateurs et peintres d'icônes, tels que N.I. Briaguine, Ia.V.Sosine, F.A.Kalikine, I.Ia.Tchelnokov, devenus ultérieurement bien connus, y commencent à travailler.

L'histoire de la restauration en Russie dans la deuxième moitié du XVIII^e et au XIX^e siècle prouve d'une manière convaincante, que les restaurateurs cherchaient à cette époque à servir les oeuvres d'art et que la restauration présentait avant tout un problème technique.

La transposition des peintures sur des nouveaux supports, le rentoilage et, un peu plus tard, le parquetage ont été mis en pratique courante. Des procédés comme la fixation des bour-soufflures par injection de colle dans une perforation faite à l'aide d'une seringue, le repassage au fer chaud, les mises

sur ton avec des pigments, broyés dans le vernis et plus claires en comparaison avec des endroits environnants, l'imitation de la peinture et de la facture de toile sur la préparation, l'utilisation des châsis provisoires - toutes ces opérations s'étaient largement répandus. Certains restaurateurs et savants mettaient en garde contre des nettoyages abusifs et des ajouts subjectives.

Au XIX^e siècle en Russie on voit apparaître des articles et des ouvrages généraux au sujet de la restauration des oeuvres de la peinture, de l'art graphique, des livres et des problèmes de la conservation.¹⁾ Ainsi dans les années soixante P. Markov avait réalisé la traduction du livre de Goupel (l'élève d'Horace Vernet) - "Guide de la peinture à l'huile suivi d'un petit traité sur la restauration des tableaux", paru à Saint-Petersbourg en 1868. L'année 1886, un grand, pour cette époque-là, ouvrage de P. Ia. Agueev "Renouvellement des tableaux à l'huile" fut publié dans la revue "Vestnik isiahtchnykh iskousstv". P. Ia. Agueev écrivait à propos de la restauration: "La reconstitution des peintures anciennes c'est une branche assez importante de la technique de peinture, aussi bien au point de vue de but de ce travail qui est à préserver telle ou telle oeuvre d'art remarquable contre la destruction et le sauvegarder pour les descendants, qu'au point de vue d'exécution qui demande une habileté toute spéciale et de la patience - des qualités qui ne sont pas propres à tous - ainsi que des connaissances profondes sur l'histoire et la technique de la peinture, la composition chimique des matériaux lesquelles le restaurateur doit employer dans son métier. En outre, cela implique une grande probité professionnelle du restaurateur, pour qu'il puisse se montrer digne de confiance accordée à lui".

Agueev soumet à la critique certaines méthodes de restauration à l'étranger, surtout celles, dont il s'agissait dans les pages du livre de A. Erkhhardt, professeur de l'Académie des Beaux-Arts de Dresde. Il met plus spécialement en garde contre "grattage" des couches picturales supérieures, rejette des procédés "secrets" et douteux de ce fait, examine des huiles, vernis, couleurs; il discute les principes de nettoyage, décrit une opération de régénération des vernis par la méthode de Von Pettenkofer, invite à étudier la chimie, la technique de la peinture dans son évo-

1) Cf. le rapport par Volkova L. et Staviski B.

lution historique.

En 1897 à Moscou on avait publié un petit manuel de Djone Brion traduit de l'anglais: "Renouvellement des gravures, dessins, plans anciens et leur recollement. Préservation et renouvellement des peintures à l'huile", où l'humidité était appelée un ennemi principal du papier et de la peinture. Naturellement, tous ces manuels contenaient beaucoup de conceptions discutables et même nocives et inadmissibles. Les techniciens manquaient de connaissances dont possède l'historien, le paléographe, l'archéologue et souvent simplement l'érudit. Ils ne se rendaient pas encore compte de ce, que l'oeuvre d'art - c'est un document historique et esthétique d'une certaine époque et qu'ils n'avaient pas le droit de la modifier. D'ailleurs, le restaurateur était d'avis qu'il pourrait dans son métier s'égaliser au maître ancien, à sa technique, à son style ainsi que faire son intervention indiscernable. Il tâchait d'obtenir une coïncidence parfaite des parties traitées et originelles, s'efforçait de s'approcher du style des oeuvres confiées à lui et s'était profondément persuadé de l'incontestabilité de ce principe. C'est ce fait qui fut la cause de ruine et mutilation d'un grand nombre d'oeuvres d'art.

Nous n'y considérons pas les méthodes de la restauration. Néanmoins, nous vaudrions dire quelques mots sur nettoyage des peintures de chevalet, étant donné une grande quantité d'oeuvres abîmées lors de cette opération, extrêmement compliquée et difficile. On pourrait indiquer les trois raisons de ce fait: l'emploi des dissolvants très efficaces, puis - l'exécution des travaux par les restaurateurs médiocres, artisans et demi-savants qui croyaient avec beaucoup d'assurance pouvoir tout faire, et enfin, - un manque presque total de connaissances concernant de comportement des résines, vernis et couches picturales sous l'action des dissolvants. Des couches superficielles s'étaient trouvées habituellement endommagées, ensuite on les commençait à repeindre et à "renouveler", après quoi on recouvrait le tableau d'un ton général, de préférence - brun en glacis. Ce ton conférait au tableau un aspect de peinture plus ancienne et masquait les traces d'intervention maladroite du restaurateur. Ce n'est que depuis de la fin du XIX^e siècle que l'application de vernis sans pigments jaunes fut mise en pratique.

Quant au traitement des supports des peintures au XIX^e siècle, nous en savons très peu. Les supports

étaient considérés souvent comme éléments secondaires de l'œuvre, et chacun pouvait en faire ce qu'il voulait. Ce n'est certainement pas un hasard, que nous rencontrons si fréquemment des cas de transposition des peintures, ayant eu des supports tout à fait sains.

La situation de la restauration des peintures murales en Russie était de même loin d'être brillante. Nous pouvons en juger sur les données d'archives, les ouvrages des historiens de l'art et sur les œuvres d'art-mêmes des années quarante du XIX^e siècle. Bref, on procédait comme suit: on nettoyait des peintures anciennes couvertes de surpeints, on éliminait des couches de crêpis détachées, en les remplaçant par un nouveau mortier, on retracait les parties manquantes du dessin de la composition, tout en respectant l'iconographie ancienne, et puis on repeignait toute l'ensemble par des couleurs à l'huile. Les fresques du II^e siècle de la Cathédrale de Sophie à Kiev en 1843-1853, les fresques de la Cathédrale de Sophie à Novgorod dans les années quatre-vingt-dix du XIX^e siècle avaient été "restaurées" par ces "méthodes". Un pareil traitement ne peut pas être appelé "restauration" - ce n'était qu'un renouvellement typique des peintures murales.

La découverte des fragments de la peinture ancienne et leur conservation - c'était un cas pas fréquent. Il faut situer son début au milieu du XIX^e siècle. Les procédés de renouvellement, dont nous venons de parler, ne sont pas nouveaux. Ils étaient déjà connus au XVII^e siècle, comme en témoignent les œuvres d'art elles-mêmes. C'était, par exemple, le cas des peintures de la Cathédrale de l'Ascension du Kremlin, restituées en 1642-1643 en respectant l'iconographie du début du XVI^e siècle.

A partir de dernier quart du XIX^e et au début du XX^e siècle tous commencent à se rendre compte de ce que le métier de restauration n'était pas conforme aux progrès de la science et de la technique.

Certains amateurs d'art et intellectuels élèvent sa protestation contre nettoyages trop audacieux exigent de mettre fin à une pratique privée des restaurateurs autodidactes - ignorants, préconisent en faveur de remise du métier de restauration sur une base d'Etat.

Au début du XX^e siècle on voit apparaître en Russie des techniciens de grande érudition dans le domaine de la restauration, bien expérimentés sur les questions d'histoire et d'art. Ce sont: I.S.Ostrooukhov, artiste

et collectionneur, I.E.Grabar, historien de l'art et peinture, Likhatchev. Dès le début ils tâchent de donner à la restauration une nouvelle orientation. Ostrooukhov à Moscou, Likhatchev à Petrograd entreprennent les travaux de dégagement de surpeints récents sur icônes, adoptent la première classification des œuvres selon leur caractéristiques de style, esquissent les deux principes de la reconstitution picturale: les retouches des parties manquantes avec un ton neutre, discernable de la peinture ancienne - pour la peinture à la détrempe de chevalet (icônes), et les retouches appliquées seulement dans des lacunes, en imitant couleur, ton et facture de l'original. En 1901 le Comité d'études de la peinture russe ancienne a été fondé. Les trois ateliers de peintures d'icônes et de restauration aux villages Palekh, Kholouï, Mstera étaient de son compétence.

Le Congrès des artistes de Russie, qui s'est tenu au mois de décembre 1911 et en janvier 1912 à Petrograd, avait nettement démontré la nécessité des réorganisations radicales.

Pour la premier fois les problèmes de la conservation et de la restauration, notamment ceux de la conservation des peintures, ainsi que le choix des matériaux de la peinture ont fait l'objet de discussion de la réunion aussi grande des représentants de l'art russe. Les questions de "restauration scientifique" ont attiré l'attention particulière.

Une série de rapports fut présenté à ce Congrès: de I.E.Répine - sur la technique de la peinture, de D.I.Kiplik - sur le vieillissement des matériaux, de D.F.Bogoslovski, - peintre et restaurateur, - sur les questions de la restauration, A.A.Moutti, restaurateur et antiquaire, - sur son expérience privé de la conservation de la peinture, ainsi que de A.Ja.Borovski, A.F.Afanasiev, A.I.Anisimov et d'autres.

I.E.Répine, parlant de la conservation des tableaux a dit que les peintres, ignorant la technique de la peinture, sont illettrés, tandis que les écoles qui n'avaient pas pu les donner des connaissances nécessaires sont criminelles. D.I.Kiplik a proposé d'assurer la protection des peintures contre l'influence de l'atmosphère polluée et tantait également à prouver la nécessité des essais de la durabilité et de la innocuité des nouveaux matériaux.

D.F.Bogoslovski révélait des causes de mauvaise conservation des peintures, en particulier des effets né-

fastes de l'humidité provoquant le détachement des couches picturales, développement des moisissures et des pourritures, la pollution de l'atmosphère et l'assombrissement de la peinture, ainsi que la destruction les supports de bois par des vrillettes; il parlait de ce que le restaurateur devait connaître la chimie de matériaux, tels comme vernis, résines, couleurs etc. Soumettant à la critique les méthodes des autodidactes, D.F. Bogoslovski a donné des caractéristiques assez précises de presque toutes les opérations de restauration employées au cours de traitement des peintures; il soulignait également la nécessité de tenir compte des cas particuliers lors de choix des procédés de restauration.

Les idées et les propositions fort intéressantes ont été également exprimé par A. Ja. Borovski, restaurateur de Péterbourg. Refutant de toutes sortes d'ajoutures et d'inventions subjectives, il s'est prononcé seulement pour les méthodes de conservation, les comblements des lacunes des fresques avec un ton neutre; il a proposé de réaliser la documentation photographique des oeuvres à restaurer par trois étapes: avant, au cours de et après le traitement et de fixer les résultats des examens et des traitements dans un livre spécial; de même il a proposé de créer la Commission d'Etat pour surveiller aux travaux de restauration, de fonder une école auprès de l'Académie des Beaux-Arts pour la formation des restaurateurs, d'éditer une revue spéciale, de réunir à l'avenir les conférences internationales des restaurateurs ainsi que des expositions systématiques des oeuvres restaurées. Toutes ces propositions n'étaient mises en pratique qu'en période moderne du développement de l'école soviétique de la conservation et de la restauration. Le Congrès a pris une résolution de recommander à tous les musées et les galeries de peinture d'avoir ses restaurateurs, et à l'Académie des Beaux-Arts - de former ces techniciens. Le Congrès a décidé également de demander le gouvernement tsariste d'accorder des ressources pour réaliser des traitements de conservation urgentes des oeuvres d'art en péril. Mais aucunes mesures effectives n'ont été pris par ce dernier et cette résolution est restée sur le papier.

Nous constatons donc, qu'en Russie, avant la Révolution d'Octobre, dans le domaine de restauration des oeuvres d'art regnaient l'indifférence et le formalisme, malgré des efforts positifs isolés; il n'y existait aucun système sévère et le gouvernement tsariste

75/12/9-12

ne prenait point des mesures nécessaires. Ce n'est que la Grande Révolution Socialiste d'Octobre de 1917 qui a donné la possibilité de mettre la conservation et la restauration des biens culturels, y compris des collections de musée, sur la base scientifique d'Etat.

I.Gorine

Directeur du VENILKR,
Président de la Section de la
restauration du Comité soviétique
de l'ICOM

ARCHIVES AND HISTORY OF DISCOVERY OF ANCIENT RUSSIAN
PAINTINGG.I. Vzdornov

USSR

In order to restore and study the monuments of the ancient russian painting special mastershops, laboratories and research institutes were organized in the USSR. Every year Soviet restorers repair and clean hundreds of icones and murals. The catalogues of the icons collections are constantly compiled in museums. The books, albums and articles devoted to medieval russian painting are published.

It is quite natural that in these collective efforts a very important part belongs to various studies of archive materials. Scientific restoration of icones and wall-paintings began comparatively late - at the beginning of XXc, that is why the archives are mainly new too. In spite of their newness they contain interesting documents with data on the investigations of the most prominent artistic monuments in the process of their restoration. The restoration of the medieval russian painting is closely connected with its general studying, that is why it is unexpedient to inspect documents of technical and scientific character separately.

Materials on problems of scientific restoration are not concentrated in a single place. There are such ma-

terials in central, regional and areal record offices, in museums and libraries, in restoration mastershops and research institutes; even in the collections of private persons. That is why it is so difficult to discover and to treat them. The work of archives investigators is the primary and important step of the collective efforts of scientists in the field of studying Russian (but not only Russian) art.

For example. In the years of the World War II in the environments of Novgorod, at Kovalevo, the ancient church of the Transformation of Saviour with the murals, dated from 1380 y. has been destroyed. Since 1964 the excavation of Kovalevo's church was commenced and thousands of fragments of painting have been found among stones and plasters. Moscow restorers A.P.Grekov and V.B.Grekova collected all the fragments of murals and combined of them original figures and scenes (as it is possible) and prepared them for museum exposition and publication.

They succeeded in restoring more than a half of murals which decorated the church before the war. This gigantic work lasted for 10 years. But without precious archive materials, photographs, descriptions, schemes and so on that work would last for an extremely longer time. Along with restoration of murals the building of the Saviour church was also restored and now, perhaps restored murals will be exhibited where they were situated before the War.

Besides documents used as subsidiary means there exist some materials with theoretical conceptions on the essence and problems of restoration as a whole; for example, these are papers, notes, draft materials and conspects of the prominent painter scientist and orga-

nizer I.E.Grabar (1871-1960). Since 1918 till 1933 he headed Central State restoration mastershops in Moscow. Though literature legacy of Grabar has mainly been published when he was alive, recently some small papers written by him and "Lecture on restoration" were discovered and published.

It is Grabar who has formulated the main concept of Soviet restoration science - as a totality (sum) of effects and means to clean and preserve suffered artistic works. The archives give us knowledge in history of restoration which started, with rough renewal of murals by painter-archeologist in the temple of S-t Sofia in Kiev and passed step by step surprisingly interesting development when russian scientists and restorers - practics have done cleaning of murals dated from XII s. in Dmitrovski Sobor in Vladimir (1918) or cleaning of bisantium icone of Vladimir's Bogomateri of XI in Us-penski Sobor of Moscow Kreml (1919).

They are of highly technical nature. History of restoration includes names, monuments towns and cloisters, long-time and difficult expeditions to observe works of art, joyful discoveries and bitter dissappointments - all of them draws a picture of development of russian painting.

In 1948 Tretyakov gallery received the documents of primary significance (Memoirs of Ukin) where almost all of characteristic features and facts of russian and soviet restoration are concentrated as in focus. In 1910-20 P.I.Ukin (1885-1945) discovered the prominent monuments, in particular, ancient icones and murals in Novgorod and Pscov.

As many other restorers of old generation Ukin grew and skilled in Mstera of Vladimir area.

In his memoirs Ukin dwelled upon the conditions of labour in pre-revolutionary masterships; he said about painters of icones in Nijnij Novgorod who renewed the icones in old tradition, about rich collectors of icones in Moscow (I.S.Ostrouhov, S.P.Rjabuschinski), about his activity in various towns of Russia.

There are few memoirs like "Memoirs of Ukin" in our achives. They are the worthy sources in history of discovery of ancient russian painting Archival materials on restoration and studying in ancient russian painting are most diverse. These are the following: official documents of state institutions on Protection of Monuments of Art and Antiquity, shorthand records of speeches of the workers of culture on common questions of restoration at the meetings and congresses, minutes of the scientific meetings and comissions on observing the repair monuments, restoration reports and expedition diaries, report notes, private and service correspondance, diagrams, photographs, colourful replicas, the sketches of icones and murals, papers and memoirs of scientists and restorers-practics, their private correspondance. Probably, manuscripts also should be mentioned as well as separate editions, bill posters and leaflet, instructions, published in small edition, notes and catalogues, small notes in magazines and newspapers.

This material could be taken into account completely if it is gathered in the special collections.

These are some thematic collections and albums with clippings in our archives. They give an idea of the organization of restoration work and museum work - particularly for the first years of the Soviet Power (1918-1928).

Studying in archives, I have been convinced that the most interesting part of the archives are the letters of course. I have in my mind not service correspondence, but private one, of the scientists restorers and public men.

In lively, ingenious manner which has little semblance to the official style. They tell each other about their discoveries, about their plans on future. These details of daily life create the background for the prominent events to which text-books and monographs are devoted. Not only a layman but even a scientist would realize the significance of the prominent events quite better if they were not artificially separated from the general course of life but imbedded into the galaxy of other lesser events and accompanied by critical judgement of contemporaries. The letters are the worthy sources. Reading them we get to know about the object at first hand. The archives on restoration work and studying ancient russian painting can be published and be a matter of concern for all those who are interested in the medieval artistic culture. The main content of these materials is researches and discoveries of ancient artistic works therefore; this content will attract attention of the widest circles of readers. Such books with these materials will be asked and read as the books about fascinating travels, about unusual natural phenomena, about archeological excavations, about gods, graves and scientists.

Taking into account the character of materials found and thinking about the possibility of their publication, I have come to an idea that these materials must be used in various manner. First of all these are the sources for general observation showing the development of

75/12/10-6

of ancient russian painting, how separate ideas transformed into special branch of science. The administration of Laboratory on Conservation and Restoration of Works of Art where I work at present has affirmed my proposal, to write "Essays on history of ancient russian painting". This book contains about 1000 pages (in typing) and must be finished by 1976.

In spite of the fact that letters are widely cited in the "Essays" an epistolary part of the archive, will be included in an original collection headed "Ancient russian painting in the letters of scientists, restorers, collectors and public men". These are the letters of those scholars who had occasion to clean icones and murals or to study them since 1900 till 1934, i.e. for the period of the most prominent discoveries. The letters of N.P.Kondakov, N.P.Lichatchev, V.N.Tschepkin, D.V.Ajnalov, V.K.Mjasoedov, N.L.Oknyev, H.I.Schmidt, P.P.Muratov, I.E.Grabar, A.I.Anisimov, I.S.Ostrouchov, N.P.Sitchev, P.I.Neradovski, V.T.Georgievski, N.M.Tschecotov, N.N.Punin and other public men were inserted in a collection.

Besides the letters where the authors touch upon the problems on russian painting I decided to include in the collection such letters in which the problems on Bysantine, Bulgarian and Serbian painting are being discussed. That is why the significant section of the collection will be correspondence of french scholar - bysantinist G.Millet with russian scientists. By the present time about 600 letters has been prepared. The archives are inexhaustible and a work will be enough for some generations of scholars. That is why I want to tell you about the prospects of publication of the archives.

In 1968 our laboratory worked out the long-term plan for collecting 12 compilations under the title "Materials and documents on history in discovering taking stock of, collecting, restoration and studying in works of russian painting". It is suggested that the main principle of collecting would be topographic one. It means that all the documents which dwell upon searching, restoring and studying in monuments of the prominent artistic centre of culture are published in one separate collection.

As a model of this collection devoted to Vologda we prepared to publish (it contains about 700 pages in typing) and materials of this collection are dated from 1920 to 1930.

To my regrett this work does ~~n~~'t last, though everybody readily grasps the significance of such investigations. There exist one more way of publishing the archives. This is collection in series headed (conditionally) "Ancient russian art" Scientific heritage". Unlike the above mentioned seria aimed at collecting of draft rough materials the second one is planned for publication of quite finished but due to some circumstances unedited studies prepared by the scientists of the XIXth century and of the beginning of the XXth century. There service correspondence and personal letters should be published as well.

As it seems to me this seria must look like as "Literature Heritage" edited in the USSR since 1933. Scientific heritage of the most prominent scientists-medieval whose articles are of great importance nowadays, must be published as a monograph. Two such collections which are combined from the most important works of Academician Grabar on Russian architecture and painting has been published.

75/12/10-8

There are many articles on restoration problems as well. The collected works of the organizer of restoration works and prominent scientist - A.I. Anisimov (1877-1939) and such collected works of N.P. Sitchev and I.A. Alsufjev is suggested to publish.

All the above mentioned plans of studying in archives could be realized if a special group which consists of qualified specialists and experienced secretaries, who types is created. It is impossible to carry out such plans alone without collective efforts.

If such a group would be created and the administration of an office who interests in our investigations would be financed our activity for 10 years, the investigators of ancient russian painting get a number of facts, new and unknown.

PRINCIPAL STAGES OF THE RESTORATION OF MONUMENTAL
PAINTING IN ARCHITECTURAL MONUMENTS OF THE RSFSR

V.V. Filatov

USSR

There are some unique items of monumental painting most of which are in the area of the RSFSR and in spite of dreadful years of the last war, that has ruined many of them, part of them are revived and being revived by restorers. They reveal more and more such monument, that were forgotten some hundreds of years ago. The development of restoration practice and scientific principles in our country are inseparably linked with state policy of protection and restoration of works of art and historical and cultural monuments as a result of victory of socialist revolution and switch over of our progressive intelligency into service of protection of artistical and cultural values that are in palaces, cathedrals and cloisters. After the February Revolution the Council on Arts attached to the Provisional Government was created. As public organizations "Union of Russian painters" and "Artistic World" took an active part in protection of monuments. But only after the October Revolution victory these efforts have obtained organizational forms in scale of whole State when in November

of 1917 under direct Lenin's directive the Board on Museums attached to the People's commissariat of Education are organized. After its reorganization and enlargement in May 1918 this Board has included into itself the Commission on protecting and revealing of works of painting. In 1924 this Commission was reorganized in Central State Restoration Studios. The main efforts of this Commission and Studios restorers were directed at preservation and revealing of monumental and easel paintings chiefly Old Russian that were in churches and cloisters. Already in 1919 one of the leading Soviet art critics N. Mashkovtsev wrote in the magazine "Hudozhestvennaya zhizn'" ("Artistic life"): "The intensive work of restorers with icons, frescos and architectural monuments, all this activity seemed so untimely, proved in fact to be a natural consequence of revolutionary progress. Due to it monuments of religion ready to become the symbol of hated past turn into values common to all mankind. The veil of legends shrouding and shading these monuments as remnants of its old meaning goes off and they appear before us in new light".

With really revolutionary boldness restorer deals with monuments sanctity of which seemed so great that even the dust accumulated on them considered to be sacred".

Since summer of 1918 restoration of painting of XII century of St Dmytrius and Assumption Cathedrals in Vladimir and also of frescos dated 1408 and executed by Andrey Rublev and Daniel Tcherny was begun. Then the works on revealing of Theophanus The Greek's and other masters of XIV century paintings were conti-

muied in Novgorod and its vicinity. At the same time the thoroughful work of revealing of iconostases painting set by the same authors and their contemporaries /of Ancient Assumption Cathedral in Vladimir, The Annuciation Cathedral in Moscow Deesises from Kashin and Serpukhov and so on/.

This first period of development of monumental painting restoration we must by rights call The Great Discoveries Era that has considerably changed our conception about skill and creation of Old Russian artists. Art historians have found revealed masterpieces for investigation by which revision of Russian art history has begun and resulted in publication of "The Russian Art History" the begining four volumes were assigned to the period before XVIII century.

In this period restorers united into public offices use for the first decade with the materials being in use during early XX century.

The loosened plaster was fastened on the wall by means of gypsum injection. Glue-tempra and powdered fresco-tempra paint layer was stabilized being impregnated with aqueous solution of gums /mainly cherry gum/ or hen egg yellow. Thus for example gum was used about 1910 for stabilisation of XVII c. wall-painting Trinity Cathedral of st Ipatius Monastery in Kostroma, and in 1918 for XII painting of St Dimetrius Cathedral in Vladimir. At the last case milk serum was used as well. In 1919 potasium glass was used for consolidation of fresco painting of early XV c. in Assumption on the Town in Zvenigorod. In early thirties it was tried to find by method of experiment more perfect glue for paint layer consolidation. It resulted in decision to

use for this end the casein glue. Since 1932 it was used for stabilisation of XII c. wall paintings in the Redeemer Church in Nereditsa by Novgorod, of 1408 in Assumption Cathedral in Vladimir and of many other monuments. The oil overpaintings were removed by means of caustic soda. But by the middle of the thirties restorers made certain of damaging effects of caustic soda, especially after partial revealing of XI century painting in St Sophia Cathedral in Kiev (representation of the prince Yaroslav's family). Their search resulted in using of the first in practice of wall-painting restoration chemically neutral solvent-dichlorethan. For the first time the XVII paintings of church Holy Trinity in Nikitniki in Moscow were revealed from oil over painting by means of paste of caoutchouc and dichlorethan. Advantage of neutral strong solvent was appreciated at once.

Perfection of methods and materials of wall-painting restoration was interrupted by the war of 1941-1945. Many monuments having unique wall-paintings found themselves in area of war operations. Especially badly they were suffered in the oldest Russian cities Novgorod, Kiev, Pskov as well as in the suburbs of Leningrad.

In 1941 - the first year of the war the Soviet Government created a commission for protection and restoration of monuments, placing on it registration of damages and deteriorations due to war as well as measures for emergency conservation. In 1943 The Main Directorate for Architectural Monument Protection attached to the Committee on Architecture of SU Minister Council was organized. During the war teams of

specialists including restorers went to front-line for inspection and urgent measures for architectural monuments and paintings in them. In 1944 by the Governmental Decree the Special Restorational Workshops were created in Novgorod, Pskov and other centers of monuments.

In 1948 number of such workshops was considerably increased by the Governmental Decree "On measures to improve the protection of cultural monuments". Restorational workshops including specialists of painting and applied arts were created and successfully work in republics, provinces individual cities.

In spite of the fact that during war and the first years of peace, as well as during years of the Civil War after the October Socialistic Revolution our country suffered from heaviest economical devastation and difficulties special necessary materials and credits were assigned for preservation of monuments (such as eggs, honey, animal and sturgeon glue that is very critical and missing materials).

During these years restorers used materials and methods elaborated in foregoing peaceful period. Facing of damaged painting with rice paper was done by means of sturgeon glue and egg yellow. Consolidation of powdered and flaking painting was performed with these materials and casein glue. Areas attacked with fungi (and there were many of such areas because the roofs were not only damaged but vaults of many monuments were brown out) were treated with solution of formaldehyde. There was a rule to treat with formalin all glued surfaces after paint layer consolidation.

75/12/11-6

Up to the early fifties for attaching of loosened plaster to masonry the gypsum was seldom used. But cavities were filled not wholly and instead of it so called "gypsum dowels" were done. It was due to the fact that gypsum used at twenties-thirties for monuments of northern and middle climatic areas turned as a result of being fresen into powder and its crystals effloresced on painted surfaces of many monuments.

In early fifties for filling of cavities lime-casein solution and solution of polychlorvynil resin in dichlorethan with porous mineral fillers (mainly pumice) begun to be used. The latter now is excluded of restorational practice due to a number of reasons. Also from methods for removing of oil overpainting on both temptra and fresco painting caustic sode was excluded and substituted with aqueous solution of amonium or with dichlorethan. Then in the late fifties combinations of neutral solvents began to be used. Since early sixties all restorers use these neutral solvents.

Last years especial attention was given to selection of materials for consolidation of paint layer for different techniques of wall-painting and different temperature and humidity conditions. The Kostroma workshop was worked out method of polyacrilamide. But a great drawback of this method is its high solubility in water and like vegetable gums it can effloresce on painting surface. It was used for consolidation of XVII c. painting in St. Trinity Cathedral of Kostroma and in this heated building has quite good result.

Since the sixties an intensive work on selection and introduction of new restorational materials was begun with the All-Union scientific research laboratory on

restoration and conservation of works of art in cooperation with Vladimir oblast restorational workshop. This long laborious work and desting in painting and architectural monuments resulted in introduction of organo-silicon compounds especially for restoration "R-15/3" for consolidation of powdered paint layer. This material and those analogous to it in contrast to all used earlier form no film, leaving painting to be permeable to air and water and at the same time quite frostresisting (the latter is of importance for the monuments of the Northern areas). Polyvinilic polymers are used to fix flaking paint layer. Of them those were chosen that form porous frostresisting film.

The new materials of high stability were used for strengthening of XII c wall paintings of St. Dimetrius Cathedral in Vladimir, of XV c in the Assumption Cathedral in Zvenigorod, XVII c of the Assumption Cathedral of Vladimir monastery of the Princess (Knyginin), XIII c and XVII c wall-paintings of the Nativity Cathedral in Suzdal, the Archangels Cathedral of the Kremlin and many others architectural monuments of the Russian Soviet Federal Socialistic Republic.

To the end of better coordination of restorational works the Ministry of Cultur of the RSFSR has created "Rosrestoration trust" that united all regional workshops under common direction.

Attainements of the last years are results of close cooperation of practical restorers and chemist-technologist working in restoration and continuous relations

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of the latter with institutions that deal with the synthesis of new materials.

A characteristic feature of present stage of development of monumental painting restoration is (beside foregoing triple unity) profound study of composition, structure and causes of destruction of monumental painting.

On this grounds a serious work on chemical and structural compatibility of materials to be introduced with materials and structural peculiarities of work of art was done. And only by this way restoration can turn from purely empirical methods into scientifically grounded ones that are able to create a sound foundation for preserving of masterpieces of the Past for future generations of Mankind.

LES ALTÉRATIONS DES BRONZES ANTIQUES EN MILIEU MARIN

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Deux découvertes d'importance capitale ont été effectuées près des côtes de la Calabre, dans la Mer Tyrrhénienne et dans la Mer Jonienne. La première, qui remonte au mois de novembre 1969, a été faite à environ 150 mètres de la côte, à 35 mètres de profondeur, à Porticello di Villa S. Giovanni, dans le détroit de Messine, et a permis de récupérer maints fragments en bronze appartenant au moins à deux statues mâles, de grandeur presque nature, dont l'une drapée, ayant la figure d'un homme âgé, qui ressemble aux philosophes grecs, tandis que l'autre, sans vêtements, à présent est acéphale; il paraît, toutefois, que la tête de cette dernière ait été volée et vendue à l'étranger. Les fragments relèvent de la cargaison d'un bateau qui a fait naufrage et remontent aux V-IV siècles av.J.C. La deuxième découverte a été accomplie en 1972 dans les eaux de Riace Marina à environ 300 mètres de la côte, à 10 mètres de profondeur; on a retrouvé deux statues en bronze, de taille plus grande, presque intactes, représentant deux guerriers, nus, dans une attitude héroïque. En principe les deux statues devraient dater du V siècle av.J.C. bien que la datation ne soit pas tout à fait certaine.

Le premier groupe de sculptures a été confié à l'Istituto Centrale del Restauro de Rome, tandis que le deuxième se trouve à présent au Centro di Restauro della Soprintendenza aux Antiquités de Florence, le travail de restauration des deux groupes de statues n'ayant pas encore été achevé.

Lors de leur découverte, la surface du bronze présentait maintes altérations, dont les plus saillantes et enlaidissantes étaient dues à d'épaisses concrétions calcaires et à des coquilles; au-dessous de ces dernières et dans les zones qui n'étaient pas affectées, ont été relevés d'autres types d'altérations dues à des phénomènes de corrosion, se présentant sous forme de patines noires, vertes, grises et rougeâtres.

Jusqu'ici seulement les altérations des fragments de Porticello ont été examinées à l'aide de la fluorescence/excitée par les radioisotopes. Ces recherches, d'ailleurs, font l'objet d'une étude qui va paraître bientôt (1). Les analyses effectuées ont révélé la présence de calcium, de soufre, de chlore, de plomb et de fer; le calcium est sous forme de carbonate, le soufre de chalcosite (Cu_2S), le chlore et le plomb sous forme de chlorures et le fer d'oxydes. Dans un échantillon on a détecté exceptionnellement la présence de chrome. Le ~~sulfure~~ de cuivre (chalcosite) est une poudre noirâtre, incohérente, très répandue à la surface du métal et semble être caractéristique de ces bronzes.

Notamment, à cause de cette particularité, j'ai été amenée à examiner la documentation concernant d'autres bronzes découverts dans des circonstances semblables, afin de vérifier si cette forme de corrosion ainsi que d'autres pouvaient être considérées en tant que caractéristiques des bronzes étant demeurés longtemps en milieu marin. Malheureusement, l'abondance des découvertes en Méditerranée s'accompagne de données techniques insuffisantes quant à la condition de la surface de ces bronzes lors de leur découverte. La plus souvent on ne dispose que de descriptions très générales dont on ne saurait tirer des conclusions; les objets relevés n'ont que très rarement été soumis à analyses chimiques et physiques avant d'être restaurés, par conséquent on ne connaît guère leurs conditions lors de leur découverte. Ainsi doit-on se borner à évaluer les conditions actuelles des bronzes, qui sont nettement meilleures que celles de bronzes ensevelis dans le terrain. Il est pourtant impossible de formuler des considérations plus détaillées. Et cela s'applique non seulement aux découvertes qui

ont été accomplies il y a très longtemps, telle que, par exemple, celle de l'Apollon de Piombino, qui remonte à 1812 et à propos duquel on signale seulement que la statue parut " toute couverte de dépôts marins" (2) et dont on décrit toutefois les différentes opérations de restauration accomplies par la suite (3), mais aussi à des découvertes beaucoup plus récentes (4).

Les concrétions dues aux sédimentations de coquilles sont parmi les altérations que l'on signale le plus souvent et qui sont également rapportées dans les premiers compte-rendus des découvertes de Mahdia (5), ainsi que de celles près du Cap Artémision (6). En ce qui concerne ces deux derniers groupes, l'on dispose pourtant de renseignements précieux en vue des études mentionnées ci-dessus. Certains fragments métalliques issus de la cargaison du navire qui a fait naufrage à Mahdia, ont fait l'objet d'analyses chimiques et ont été signalés dans un brillant rapport de Lacroix, paru dans les Compte-Rendus de l'Académie des Sciences de Paris (7). Lacroix étudie des feuilles en plomb tirées de la coque du bateau et des clous en cuivre, creux. Il constate que les objets en plomb sont caractérisés par la formation de sulfure de plomb dans la couche superficielle, tandis que dans les plis de ces feuilles on relève la présence d'un minéral incolore avec du plomb et du chlore, la cotunnite (PbCl_2), que l'on retrouve à l'état naturel dans les fumerolles du Vésuve et dans un gisement de métal à Tarapaca (Chili). Les clous en cuivre creux, au contraire, à l'extérieur sont couverts de sulfures et de bryozoaires (coquillages), tandis qu'à l'intérieur des cavités géodes le métal est intact avec quelques cristaux transparents et brillants de phosgénite ($\text{PbCO}_3 \cdot \text{PbCl}_2$). Les clous qui sont encore enfoncés dans le bois ont été complètement transformés en sulfures à la suite d'un processus qui s'est produit à partir de l'extérieur; il existe deux types de sulfures, la covellite (CuS), qui est le minéral prédominant, d'une couleur bleu indigo, ayant une lueur métallique, et la chalcosite (Cu_2S) de couleur noirâtre. D'après Lacroix c'est le premier processus d'altération qui donne lieu à la formation de chalcosite et celle-ci se transforme ensuite en covellite. Toujours d'après Lacroix les phé

nomènes de sulfuration du plomb et du cuivre sont dus à la présence de matières organiques, notamment au bois de l'épave (8).

Une autre étude intéressante du point de vue chimique a été effectuée à l'occasion des éclatantes découvertes marines accomplies à plusieurs reprises près du Cap Artémision, ainsi que de la découverte de l'éphèbe de Marathon. L'auteur en est G. Zenghelis (9), lequel, cependant, n'a pas su interpréter correctement les résultats obtenus à cause de la dichotomie existant entre patine artificielle et patine naturelle, ce qui, à l'époque, était le problème dominant. Entre autres Zenghelis signale que, lors de sa découverte, l'éphèbe de Marathon (10) était revêtu d'une croûte noire, parfois luisante, et d'une couleur pourpre foncée; il nous rapporte aussi les données concernant les résultats de l'analyse de cette croûte: Cu 92%, Sn 6%, S 4,2%. Par contre l'analyse du bronze avait donné les résultats suivants: Cu 88,5%, Sn 9,2%, S 2%. La teneur en soufre était d'environ 4,5% dans la barbe du dieu de l'Artémision et atteint 13,7% dans le sabot du cheval également découvert près du Cap Artémision (11) et qui présentait aussi une patine noire. La teneur élevée en soufre a été expliquée par Zenghelis comme due à l'exposition à des vapeurs sulphydriques de la part de l'artiste ancien en vue d'obtenir une patine artificielle; en réalité il s'agit du même phénomène que l'on constate dans les bronzes mentionnés ci-dessus.

Les reinsegnements portant sur les autres découvertes importantes en milieu marin ne sont que vagues et de caractère général: l'éphèbe de Cythère, découvert en 1900 et restauré à Paris par André, a été nettoyé de sa patine et couvert d'une peinture noire (12); l'Apollon de Salerne qui, lors de sa découverte était orné par une belle patine vert foncé (malachite?) avec des taches bleuâtres (azurite?) fut nettoyé pour le dégager des incrustations et peint par la suite d'une patine grise foncée (13). On ignore les circonstances de la découverte du Poséidon de Livadostro, sauf qu'il a été retrouvé en pièces (14), tout comme on ne connaît guère les conditions de la Dèmèter de Bitez (15).

Ce n'est qu'après la découverte du complexe dit du "Grand Congloué", à Marseille, que l'on signale encore des faits se rattachant à ceux dont j'ai parlé. Les a-

analyses effectuées par M.me Weill sur des éléments en plomb et en cuivre de l'épave témoignent de la transformation du plomb en sulfate de plomb (SO_4Pb) dans la partie en contact avec le cuivre et en sulfure de plomb dans celle en contact avec le bois, sous forme d'une matière noire, volatile et pulvérulente. Le clous en cuivre, par contre, ont été presque tous transformés en oxyde de cuivre (CuO , Cu_2O) et en sulfure de cuivre (Cu_2S). Dans ce cas, également, la corrosion est attribuée à l'action des sulfobactéries qui se sont développés dans le bois (16). L'action de ces bactéries, notamment celle du desulfovibrio sur des métaux plongés en mer, à fait l'objet d'études récentes et est considérée comme une composante fondamentale des phénomènes électrochimiques de corrosion en milieu marin. Les bactéries sont aussi responsables de l'augmentation du Ph, et, par conséquent, d'une altération dans l'équilibre entre carbonate de calcium et bioxyde de carbone, donnant lieu à la formation de carbonate de calcium insoluble et d'hydroxyde de magnésium: ce sont ces deux derniers minerais qui développent des concrétions épaisses où se cachent des cailloux et des coquillages, caractéristiques des métaux longtemps demeurés dans l'eau de mer.

Le fait que tous ces phénomènes soient typique du milieu marin et qu'ils ne se produisent pas en eau douce, pourrait être démontré par les résultats des nombreuses analyses effectuées sur les bronzes et les fers des navires de Nemi (18), qui sont sans aucune trace de soufre, ni de sulfures, de calcium ou de carbonates.

Ainsi pourrait-on conclure que la fréquence élevée de ces deux types d'altérations, très probablement dues à l'action des sulfobactéries, est particulière des bronzes marins. Par contre, probablement à cause de l'atmosphère pauvre en oxygène, sur ces bronzes est beaucoup moins intense la corrosion due à l'action des chlorures.

Je ne saurais terminer cet exposé sans insister, même si cela pourrait sembler inutile, sur le rôle capital des examens scientifiques à effectuer dès que l'objet a été découvert; si une étude de ce genre avait été systématiquement conduit dans le passé, si la description de l'archéologue avait été accompagnée du rapport du physicien et du chimiste dans les domaines de leur compétence, au lieu de données insuffisantes, aujourd'hui l'on

disposerait d'une masse considérable d'informations statistiques portant sur les conditions des objets lors de leur découverte, sur la composition des alliages et des patines, sur les techniques de travail, sur les altérations des bronzes anciens: ce qui nous permettrait d'aborder les problèmes de la conservation avec beaucoup plus de confiance et nous aiderait mieux à définir l'histoire de la technologie, qui est un des aspects les plus passionnants de l'histoire du progrès et de l'évolution de l'homme.

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 - (2) Raoul Rochette, Ann. Inst., 5, 1833, p.323.
 - (3) Ces données ont été recueillies dans: B. Sismondo Ridgway, The Bronze Apollo from Piombino in the Louvre, Antike Plastik, VII, Berlin, 1967, pp.43-75, faisant état aussi des résultats des analyses récemment effectuées aux Laboratoires du Louvre.
 - (4) La liste des découvertes en mer jusqu'à 1930 se trouve dans: A. Merlin, Submarine discoveries in the Mediterranean, Antiquity, 4, 1930, pp.408-414.
 - (5) A. Merlin, C.R.A.I., 1907, p.317; 1908, pp.245-254; A. Merlin, L. Poinssot, Mon. Piot, 1909, p.31, n.1; pour les problèmes archéologiques voir: W. Fuchs, Der Schiffsfund von Mahdia, Tübingen, 1963.
 - (6) N. Bertos, Αρχαιολογικὸν Δελτίον, x, 1926 (1929), p.87; Ch. Picard, Manuel d'archéologie grecque, Paris, II, 1939, p.63. Les jambes avaient été restaurées dans le passé et on pouvait y voir une âme en bois.
 - (7) M.A. Lacroix, Sur quelques minéraux formés par l'action de l'eau de mer sur les objets métalliques romains trouvés en mer au large de Mahdia (Tunisie), Comptes Rendus hebdomadaires Académie des Sciences,

151, 1910, Paris, pp.276-279; R.J. Gettens, Patina: Noble and Vile, Art and Technology, M.I.T. Cambridge, Mass., 1970, p.59.

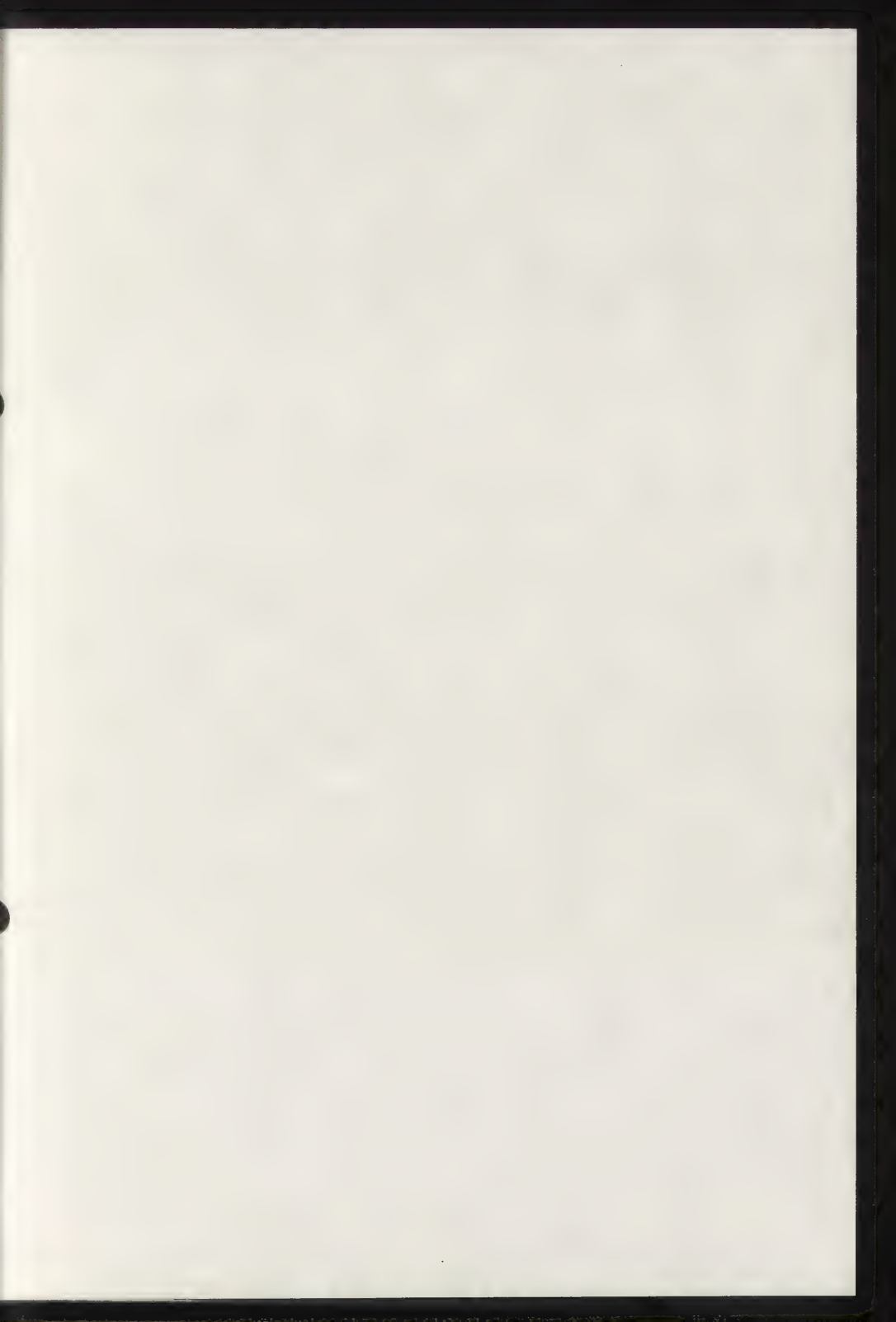
- (8) Dans les études de Daubrée et Lacroix (Minéralogie de France) on signalait la transformation en chalcosite du cuivre de certaines monnaies romaines jetées comme offrandes dans les eaux thermales; mais on avait attribué cette transformation à l'hydrogène sulfuré présent dans les eaux, bien que l'on aurait pu songer même à l'action des débris organiques présents en quantité considérable.
- (9) G. Zenghelis, Contribution à l'étude des bronzes antiques, Museion, III, 1929, pp.113-127; J. Charbonneaux, Les bronzes grecs, Paris, 1958, p.6.
- (10) Picard, Manuel, III, 1, pp.498-509; Pour les premiers renseignements et une photo avant la restauration voir: K.A. Rhomaios, Ἀρχαιολογικὸν Δελτίον, 9, 1924-25 (1927), pp.144-187.
- (11) Dans le sabot du cheval d'après Zenghelis on trouve les teneurs suivantes: Cu 64,8%, Fe 1,1%, O 0,18%, matières insolubles 2,4%.
- (12) Zenghelis, op.cit.; P. Cornelis Bol, Die Skulpturen des Schiffsfundes von Antikythera, Mitt. Deutsch. Arch. Inst. Ath. Abt., 2 Beiheft, 1972.
- (13) D. Mustilli, L'Apollo di Salerno, Bollettino d'Arte, 1937, pp.136-147.
- (14) D. Filios, Ἀρχαιολογικὴ Ἐφημερίς, 1899, cc.58-74; Picard, Manuel, II, 1, p.155.
- (15) G.E. Bean, Illustrated London News, Nov.7, 1953, pp.747-749; il dit simplement que la magnifique statue du IV siècle découverte en mer près du village de Bitez, près de Bodrum, l'ancienne Halicarnasse, à présent confiée au musée d'Izmir, était défigurée par des "petrified marine worms".
- (16) A.R. Weill, Analyse des pièces métalliques en cuivre et en plomb provenant de l'épave romaine dit du Grand Congloué, La Revue de Métallurgie, 51, 1954, pp.495-566; F. Benoit, L'Epave du Grand Congloué à Marseille, XIV, Suppl. Gallia, C.N.R.S., Paris, 1961, pp. 193-194. A propos de la formation des sulfures:

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R e s u m é

A l'occasion d'une étude portant sur les altérations de deux groupes de statues récemment trouvées près des côtes de la Calabre l'auteur a eu l'opportunité de reconsidérer les données concernant d'autres bronzes étant longtemps demeurés en milieu marin.

Quoique les recherches effectuées par le passé soient assez insuffisantes par rapport à l'abondance des découvertes, d'après les données recueillies on peut toutefois conclure que la transformation du métal en sulfures et la formation de carbonate de calcium insoluble sont parmi les altérations qui se produisent le plus souvent. Ces altérations relèvent de l'action des sulfobactéries, qui se développent parmi les débris organiques, c'est-à-dire dans le bois de l'épave, et semblent être caractéristiques des bronzes de provenance marine.



ON-SITE CONSERVATION REQUIREMENTS FOR MARINE ARCHAEOLOGICAL EXCAVATIONS

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Abstract

Many marine archaeological excavations are carried out in isolated areas, many kilometres from the facilities of a conservation laboratory. It is important that objects excavated from a wreck are stored in a stable environment until they can be transported to the laboratory. In addition, the marine archaeologist often requires an object to be cleaned for identification purposes. The conservator also requires that storage and preliminary conservation procedures will in no way harm the object or cause problems when the objects arrive for treatment at the laboratory.

The procedures for on-site conservation are discussed in relation to the position and nature of the archaeological site and the requirements of both the marine archaeologist and the conservator. The recommended techniques for the on-site conservation of the different materials likely to be recovered from a wreck are described, but it is concluded that the most important requirement is for a full-time on-site conservator to be responsible for all conservation work, and who will return to the Laboratory with the material at the end of the expedition to organise the conservation of the material. This will ensure that there is a flow on from the field into the laboratory for the treatment of the recovered material.

Introduction

To quote one of the worlds leading marine archaeologists "It is only all right to raise material if you know how to conserve it" (1). This in fact should be taken a step further because conservation commences the minute the environment of an object lying on the sea bed is changed in any way whatsoever, and the requirements should therefore include not only laboratory conservation facilities but also on-site facilities. It is rare that a marine archaeological site is situated adjacent to a

Conservation Laboratory, perhaps the instance of the Wasa is the rare example, and even if the site is within only a few hours of a Laboratory this is sufficient time for excavated material to deteriorate, often with disastrous results, unless conservation processes are applied immediately.

For the past three years the Department of Maritime Archaeology of the Western Australian Museum has been carrying out extensive excavations of the Batavia (2) which was wrecked in 1629. Due to the remoteness of the wreck site the problems and requirements for on-site conservation are extreme and our experiences will now be discussed from the view point of both the archaeologist and the conservator, followed by recommended on-site conservation procedures to be carried out for the different types of material likely to be found on a wreck site.

Problems of the wreck site locality

The coast line of Western Australia stretches for 7,000km. It has numerous coral reefs and is infamous for the lack of safe anchorage for ocean going vessels. Some of these reefs are close to the mainland, for example the wreck site of the Vergulde Draeck (1656) is only 5km out to sea. However, that of the Batavia is 56km from land also 480km from the Western Australian Museum Conservation Laboratory in Fremantle. Fortunately the Batavia was wrecked only 3km from a small island - Beacon Island, upon which has been established the excavation headquarters.

An expedition is usually restricted to approximately 5 months each year due to finance and the weather conditions the ideal time being from December to May. At least 5 people are required to effectively run the expedition and this requires a constant supply of food, fuel, chemicals and other essential items. Only from mid-March when the cray fishing season is in operation does a supply boat call in at the island. At other times the Museums' work boat has to be used to travel to Geraldton (56km) on the mainland which often takes 3 days. This can be very frustrating, especially if those days prove to be good diving days.

There is no supply of water on the island apart from rain water tanks, and as the annual rain fall is only 500mm the 22,000 litre storage tanks have to be supplemented by imported fresh water. A shower in fresh water is unheard of and often those recovered relics which require storage in fresh water have priority over the archaeologist.

It is essential that very careful preplanning is carried out prior to an expedition as it can be very costly and time consuming to bring in items that have been forgotten. Even though items can be freighted to

the island by float plane this is both expensive and is limited by the capacity of the plane. Because it is often difficult to predict which conservation facilities will be required it is usual to attempt to foresee all possible requirements even if this results in chemicals and other materials remaining unused.

The three main factors which determine the requirements for on-site conservation are the weather, remoteness and finance. It is not possible to send every recovered item immediately to Fremantle for conservation as the costs would be enormous. As the weather has to be reasonably good for excavation work many days are wasted and this is why an excavation programme of 5 months is in fact at best only 3 working months. For these reasons it is necessary for the excavated material to be stored on the island often for the duration of the excavation, after which it can all be transported by sea to Fremantle in one swift and relatively cheap operation. This is particularly important for the large ships' timbers which are at present being excavated.

The island itself causes problems. It is a low coral island, only 3m above sea level, and is 2 hectares in area with no vegetation apart from low scrub. There is therefore no natural shade and it receives an average of 8 hours of sun per day. It is extremely difficult to dig storage tanks in coral, and polythene sheeting can only be used with great care because of the likelihood of tearing on the sharp coral. At high tide the water level rises to within 2m of the surface of the island, restricting the depths of tanks.

As mentioned previously the weather is not conducive to stable storage, no natural shade, long hours of sun each day, temperatures ranging from 17°C to 40°C and relative humidities from 50 to 70%.

Requirements of the marine archaeologist

As soon as relics are removed from a wreck site it is important that the marine archaeologist is able to work with them. They must be registered, described, often drawn and photographed, however, at no time during these procedures must they be allowed to deteriorate. These procedures on an isolated site like Beacon Island are an essential part of the life of the expedition. The weather often prevents work on the actual site and the time is then spent on recording etc. This firstly keeps the archaeologist fully occupied and it also ensures that the recording is up to date with the excavation work.

The archaeologist is also, and quite naturally, keen to identify an object he has just recovered. If it looks interesting he will not wish to wait perhaps 5 months until it has been cleaned at the conservation laboratory. However, what he does must be carefully

controlled and be a basic part of the conservation treatment for any particular item. It is also important to identify to some degree items such as coins. On the various Dutch East Indiaman wrecks quantities of silver coins have been found and although many of these are the same, there are some very good and rare examples which are often to be found in particular pockets on the wreck. Silverware from the Batavia when first recovered was thought at that time to be a piece of battered pewter. Later excavations in the same area revealed a number of very important items of 17th century Dutch silver. Therefore it is important to the archaeologist that he knows what he has excavated.

The same reasoning can apply to sherds. It is important that broken ceramics are temporarily reassembled to check if all pieces are there, if not then a more intensive search can be carried out on that particular site. Again this temporary restoration may involve both partially cleaning the ceramic pieces and fixing them together, at all times not allowing the ceramics to deteriorate, which means essentially that they must be kept wet.

Many large concretions are recovered from a wreck site and they may or may not contain valuable relics. It would be very difficult and expensive to store all these concretions and transport them to Fremantle for radiographic examination prior to opening them up. The Vergulde Draeck excavations did allow concretions to be transported to Fremantle and in one season over 20m³ of rubbish was thrown out. To handle and transport this from Beacon Island to Fremantle would have been an expensive and wasteful operation.

It can be seen, therefore, that the archaeologist will want to work with his material as soon as it is recovered and this will require primary conservation procedures to be carried out.

Requirements of the conservator

It is important that the conservator is fully involved with all on-site conservation and restoration procedures. He is the person to recommend which procedure should be used for the particular requirement of the archaeologist. He must also have the detailed records of all procedures carried out on the individual items. It is essential that objects are stored or handled in a manner which will cause least damage to them. The storage environment must be stable, and a shallow tank of sea water on an exposed island is far removed from that on the sea bed 10m deep. The conservator ideally would prefer as little as possible done with the objects but where treatments are required it should be his decision and advice not that of the archaeologist. If procedures are well organised then the 5 months on the island can be a large

part of any prolonged conservation process, especially those of desalination, if fresh water supplies allow.

It is therefore essential that there is a conservator on-site during the entire season of excavation. He should be responsible for all conservation advice and procedures, and also related recording. He will be fully capable of recognising different types of metal, ceramics and other materials. We have experienced examples of fine Italian lace from the Batavia looking like a piece of seaweed, and as mentioned earlier, pewter mistaken for silver. Some ceramics such as low fired terracottas are very difficult to handle as they tend to readily revert to clay, whereas high fired stoneware can be handled quite safely.

It is important that the correct conservation procedures are used for cleaning objects - the use of a wrong chemical and an object may be irretrievably damaged. The wrong adhesive used with wet ceramics has in our experience caused damage to the fragile edges of the join and the adhesive has proved very difficult to remove. The result was extensive restoration requirements.

In addition to having on-site conservation advice and expertise there is another advantage, that of the follow-up at the Conservation Laboratory at the end of the excavation season. The on-site conservator can provide more than documentary evidence of the procedures used and these will ensure that the conservation procedures then carried out will be correct for the particular material and circumstances.

On-site conservation procedures

1. Metals

1.1 Iron.

The rapid deterioration of iron objects recovered from the sea is well known. On the sea bed the objects have reached a steady state as regards their corrosion. Covered by coral the oxygen and chloride ion content at the metal surface will be reasonably constant. However, as soon as they are removed from this environment and exposed to the atmosphere then fresh, rapid and irreversible corrosion occurs. Cannon balls have been seen to explode and hemp wadding from the bore of a cannon to commence to smoulder (3). It is therefore essential to retain as much concretion on the removed iron object as possible and also to exclude oxygen. This is usually achieved by keeping the object wet, which will also prevent the concentration of chloride ions building up which is another aggressive agent for iron. These precautions should be carried out immediately the iron object is brought to the surface. It cannot be left on the exposed deck of a work boat for even a few

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minutes as it could begin to deteriorate. Therefore large objects should be wrapped in sacking and keep continuously hosed with water. Small objects should be immediately immersed in a container of sea water.

On return to the expedition headquarters the iron objects must be stored in a stable environment. If they are still completely encapsulated in coral then they could simply be immersed in seawater. However, many objects have been partially exposed when excavated and these will deteriorate if stored in sea water. For these and all other objects which have been cleaned of coral the best environment is an alkaline one in the pH range 10-13 using 0.5 M sodium carbonate or 0.1 M sodium hydroxide solution. Iron will not deteriorate in these solutions even if the chloride content is high. As fresh water is usually not available, a solution of 20gm of sodium hydroxide per litre of sea water is a suitable storage environment. The extra benefit of this solution is that some of the chlorides in the iron will be removed during the process reducing the time required to later stabilise the iron by a full conservation process. This procedure can be carried out for small and large iron objects although it is difficult with cannon and anchors due to the requirement of large storage tanks. This problem has been resolved to some extent on Beacon Island by storing large objects in a deep natural hole in the coral reef near the end of the jetty to the island. Great care must be taken in storing large objects under the sea as the movement of sand and water may create a very erosive environment - the storage site should only be chosen after careful inspection. Also, the objects must be well protected by concretion.

Small and fragile iron objects can be stored in a dry atmosphere. The use of a desiccating agent such as self indicating silica gel is sufficient to prevent further deterioration. Any object stored in this environment must be cleaned of coral as this will harbour moisture and chloride which will tend to cause fresh corrosion.

Care must be taken in removing concretions from iron objects as there is the danger of damaging the remains of the underlying material. This will be discussed later in more detail.

With iron objects, especially cast iron, it is therefore essential to keep the object wet at all times after recovery and to exclude oxygen. If prolonged storage is required then an inert environment must be chosen, depending on the size and condition of the object.

1.2 Copper and alloys.

Copper and its alloys, essentially brass and bronze,

do not deteriorate rapidly in a saline environment unless by erosion or under the accelerated attack due to an unfavourable galvanic couple. Upon excavation, copper will not deteriorate rapidly upon exposure to the atmosphere and can be allowed to dry out. However, if storage is required for some time it is advisable to store in either fresh water (or sea water if fresh water is not available) or in a dry atmosphere using silica gel as the dessicant. This is to ensure that there is no corrosion of the copper by what is known as 'bronze disease' (4). This appears to require a humid environment and oxygen for the formation of hydrochloric acid which reattacks the metal in a cyclic corrosion process. In water, any acidity is rapidly neutralised and in a dry atmosphere the acid will not form.

If it is important to clean objects for examination then a 10% solution of citric acid containing 4% thiourea as inhibitor can be used. Care must be taken in cleaning these objects as brass and bronze can become mineralised after prolonged exposure to seawater, leaving an often porous and in some cases a brittle and in other cases a relatively soft matrix. Therefore, careless handling could easily damage these objects. If cleaned of all concretion and corrosion products the objects can be stored dry because the chlorides required for the formation of 'bronze disease' will have been removed. However, if only partial cleaning has been carried out then again either a completely dry or an aqueous environment is necessary.

1.3 Lead and its alloys

Lead objects are not usually very heavily concreted and will normally not require on-site conservation. The objects can be stored dry and no other precautions are necessary.

It is advisable not to attempt to clean pewter objects in the field as these often contain pustules of tin oxide which if removed will leave a hole in the object which if badly affected by this form of corrosion could completely disintegrate. It is advisable to store small lead and pewter objects in a polythene bag to protect them against organic acid vapours which cause rapid corrosion.

1.4 Silver and gold

Silver and gold objects can be stored dry and no special precautions are necessary. However, care should be taken with preliminary cleaning of such objects in the field.

The concretion can be cleaned from coins in a 10% solution of either citric or formic acids. This will usually yield sufficient detail of the object to enable its identification. However, if further cleaning is required then coins should be cleaned by electrolysis

(5) in a 2% solution of sodium hydroxide using stainless steel sheets as the anode. A battery charger which supplies 6 volts and 3 amps will be adequate for this type of work. However, here again it is important that a careful examination of the object is carried out before the electrolysis treatment is commenced. Silver can also become mineralised by exposure to seawater due to the preferential leaching out of copper (the usual alloying agent of silver) and can be left in a brittle state. The evolution of hydrogen which normally accompanies electrolytic reduction can damage a fragile piece of silver and in some instances silver coins have been known to separate into layers during this process.

2. Ceramics, Glass and Stone

Ceramic, glass and stone objects must not be allowed to dry out, otherwise salts crystallising out in the body or the glazes of ceramics will tend to cause physical damage. The objects should therefore be stored in seawater containing a fungicide (for example 20ppm Panacide, available from British Drug Houses) to prevent fungal growth. Fresh water or deionised water should not be used for immediate storage of ceramics otherwise osmotic pressures set up in the objects could again cause damage.

However, if fresh water is available the washing procedure for ceramics can be commenced. The salinity of the water is slowly reduced over about a month, to that of fresh water, and a month later deionised water can be used. This will reduce the time for desalinating ceramic or glass objects once they reach the laboratory. Care must be taken with ceramics because the low-fired earthenwares tend to revert to clay if mishandled, also the glazes are likely to be friable.

The large number of building blocks (27 tonnes) recovered from the Batavia during the 1973-74 expeditions were stored dry on Beacon Island but only after tests showed that there would be no danger of fretting or exfoliation when the salts crystallised out.

When it is important to clean the object immediately, mechanical means must be used as acid treatments tend to cause deterioration. If concretions are not allowed to dry out they remain reasonably soft and can be removed with a dental pick or vibrating air pen.

In order to check that all the pieces of a broken pot are present it is necessary to reconstruct the pot temporarily. This can be done using a PVA adhesive (UHU - Werk H.u.M. Fischer GmbH H. D - 758 Buhl, Baden, W. Germany) which will adhere to wet sherds and does not shrink appreciably when dry. It also retains slight flexibility thus reducing the tendency to cause mechanical damage to fragile edges. The adhesive is readily

soluble in acetone.

After cleaning and reassembly if necessary, the ceramics are returned to the appropriate storage environment.

3. Wood, ivory, bone and leather

Organic materials including wood, ivory, bone, and leather must always be stored wet. Here again a seawater environment containing a fungicide is necessary to ensure that the materials will not dry out thereby shrinking and cracking. Although the majority of bone and leather items are small, wood and ivory can cause a problem due to the size of the object. The current Batavia expedition is raising the remains of the hull timbers which are up to 4m in length and 1m thick. Elephant tusks 1.5m long have also been recovered from the Vergulde Draeck. These are stored by two techniques. A large hole about 2m deep is dug in the coral island (limited in depth by the high tide mark), lined with sand and then thick polythene sheet. The timbers can safely be stored in this tank containing seawater and a fungicide and are covered with black polythene sheet which also helps to prevent fungal growth. Although this "black body" will create higher temperatures, provided there is no leakage of water the timbers will not deteriorate. A less satisfactory method is to store the timbers in a thick walled polythene sleeve, also containing seawater plus fungicide. Unfortunately, it is not possible with these to achieve complete immersion of the timbers and in the very hot conditions on Beacon Island dehydration has been found to occur. This has been partially alleviated by the construction of shelters to create shade over the timbers stored in the polythene sleeves.

Concretions

Many large concretions are removed from a wreck site and these may or may not contain valuable objects. It is virtually impossible to have an on-site field X-Ray unit due to the numerous problems involved, and the choice therefore lies between storing all concretions in seawater and the expense of transporting them to the Conservation Laboratory for correct examination, against opening up the concretions on-site. Due to the large expense involved the majority of concretions are opened up on site. This is done mechanically by the aid of compressed air driven tools. These range from a rivetting gun, which contains different shaped blanks for various tasks, down to a fine air pen. In all cases the amount of pressure which can be exerted by the tool can be carefully controlled.

Experience has shown that the majority of concretions contain nothing of significance although great care is taken with those containing the remains of iron objects,

as these can be used as moulds for taking plastic replicas of the original contents (5). A valuable piece of concretion was recovered from the Batavia several years ago. This contained the remains of sets of leather-lined iron breast plates. The iron had completely disappeared but the leather survived reasonably well. The concretion was used as a mould to make a replica of the breast plate and with the use of metal powder impregnated polyester resins this produced an excellent replica of the original object. The concretions produced perfect moulds for this work and there were in fact large areas of gilding from the original iron breast plate still preserved in the concretion.

Transportation

All objects must be transported to the Laboratory in the same storage environment as they are held at the expedition site. Small iron objects such as cannon balls, can be transported in 2% sodium hydroxide solution contained in a 200l drum. Larger objects must be wrapped in sacking, well soaked again in sodium hydroxide solution and then covered with plastic. Cannon are then packed in wet sawdust in a polythene-lined wooden crate for transportation. This is not possible with anchors, however, which are transported wrapped in canvas and plastic.

Other delicate objects such as ceramics, are first sealed in a polythene bag containing the seawater/fungicide storage solution. They can then be carefully packed in the usual manner to prevent breakage.

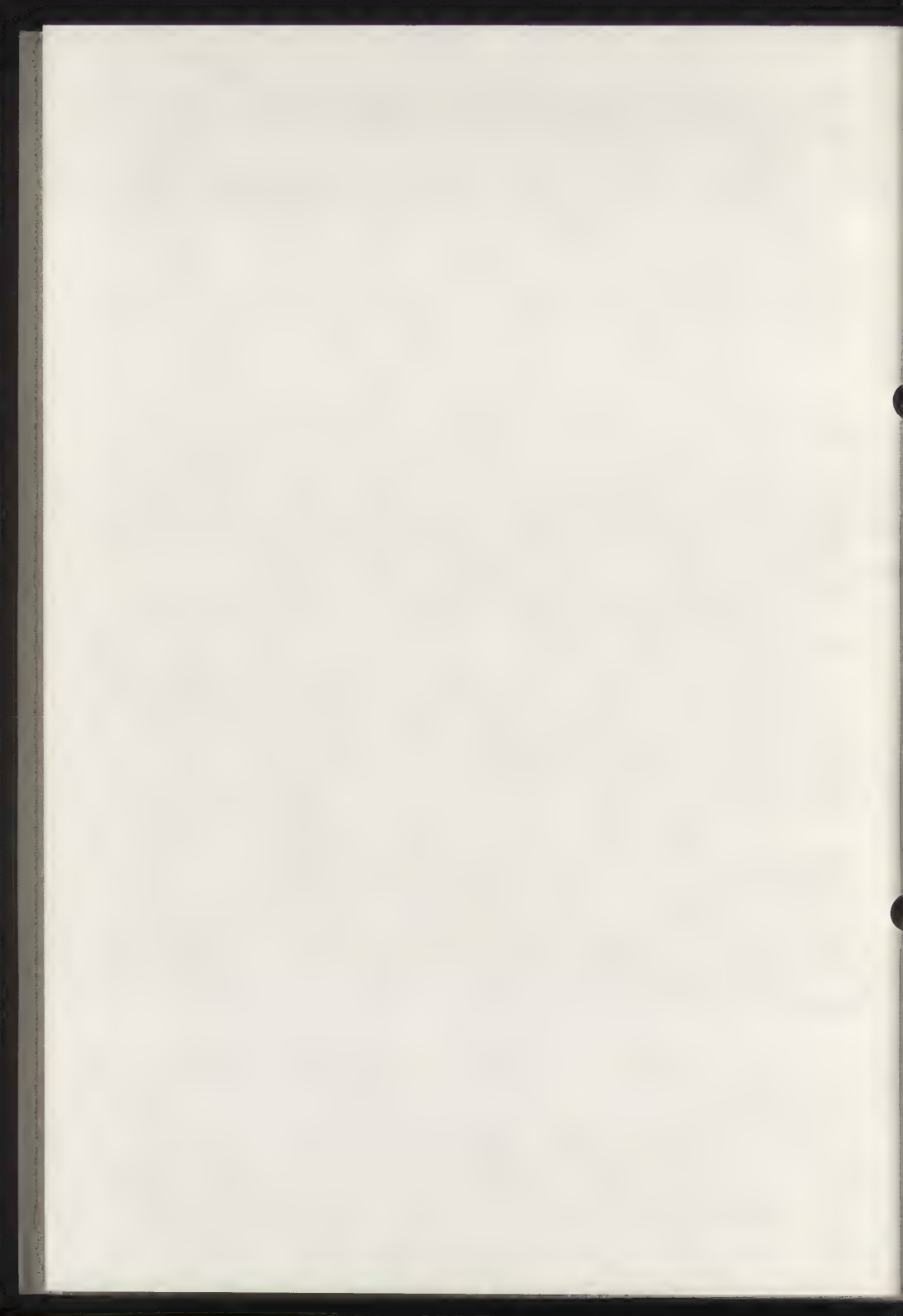
Large objects such as ships' timbers are sleeved in polythene tubing and sealed in with a seawater/fungicide solution. As these will be held in this condition for only a few days there is little danger of deterioration due to dehydration effects.

It is again important that both speed and care are taken during transportation which might involve ship, rail, road, air or a combination of these. The less handling carried out the better. Immediately upon arrival at the Conservation Laboratory the objects are registered, their condition recorded, and they are then placed in the same storage environment used at the expedition site. From then onwards normal conservation procedures can be carried out.

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ALKALINE SULFITE REDUCTION TREATMENT OF MARINE IRON

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Abstract

The chlorides present in the corrosion region of marine iron were found to be predominately iron oxy-chloride (FeOCl). The kinetics of chloride release from marine iron into wash solutions at various pH and temperature were determined experimentally and a mechanism was proposed. Working from this mechanism a process was designed to maximise the efficiency of washing techniques for treatment of marine iron. This process, which involved washing in a hot alkaline sulfite solution, was investigated, and its efficiency in the removal of chloride and its effect on the corrosion products of marine iron were determined.

Introduction

The stabilization of iron objects recovered from the sea is one of the most difficult problems encountered in marine conservation work. In the past, a number of different methods have been proposed for treating marine iron but at present only two methods, alkaline electrolysis and high temperature hydrogen reduction, appear to be in general use. Neither of these methods is completely satisfactory. Alkaline electrolysis is a very slow process and there is the danger of surface layers exfoliating due to hydrogen formation on the underlying metal. High temperature hydrogen reduction causes irreversible changes in the metallurgical structure of the iron and in addition the equipment required is often beyond the financial capacities of smaller laboratories. With these points in mind we have attempted to develop a treatment method for marine iron which would be rapid, effective and require only limited equipment. The alkaline sulfite reduction treatment described here appears to meet these requirements although, at the time of writing, long term exposure tests on treated articles have not yet been completed.

Determination of rates of chloride removal

The main requirement in the stabilization of marine iron is the removal of the chloride contained in the corroded regions of the object. It is well known that the concentration of these chlorides can be reduced by washing the objects in low chloride solutions and this has formed the basis of some treatment methods used in the past, without great success (1,2). To obtain a complete and rapid removal of the chlorides using a washing treatment it is necessary to know which factors influence the rate and extent of chloride removal and then, using this knowledge, devise a system which has maximum efficiency.

The effects of pH and temperature on chloride removal from corroded marine iron were determined using matched iron samples. For a given wash solution the rate and extent of chloride release will be controlled by the nature of the solid, in particular by the amount of corrosion product, the initial concentration of chloride in the solid, the porosity and the shape of the corrosion layers. To determine any effects due to changes in the wash solution it is necessary to maintain all of these solid derived factors constant; i.e., the solids should be identical or as near as is feasible. This was achieved by taking each of a set of samples from adjacent regions of an iron object, and then checking the samples for similarity of size and weight, and for depth, pattern and structure of their corrosion products. These samples were then washed in solutions at different pH or temperature and the variations of the rate and extent of chloride release for samples within each set were compared. For the reasons given above, comparison of samples from different sets is not valid.

Figure 1 shows the concentration of chloride in the wash solution, against time, for a pair of matched samples at pH of 4.8 and 12.1. Two important points are illustrated in this figure. Firstly, the rate of increase of chloride in the wash solution follows

a logarithmic law of the type $[Cl^-] \propto e^{-kT}$. This type of rate law is characteristic of first order reaction. Secondly, the final concentrations of chloride in the wash solution are a function of the pH of the wash solution. This demonstrates that the system is approaching an equilibrium whilst an appreciable amount of chloride still remains in the solid. Any theory for the chloride removal by washing must take these two factors into account.

Before speculating on the mechanism of chloride removal it is essential to determine the nature of the chlorides in the corrosion product. As some of the

corrosion products on iron objects recovered from the Batavia (1629) contained 13-14% chloride by weight, it was possible to determine directly the form in which the chloride was present from the X-Ray diffraction patterns. The results obtained are shown in Table I and these show that FeOCl is the major chloride containing compound in the corrosion products rather than the more generally assumed FeCl_3 or FeCl_2 .

During washing the chloride is released according to the reaction



When this is considered as an equilibrium with the rate determining step in both directions being first order with respect to all the participating species, then equation 2 for the concentration of chloride in the wash solution at time t is derived (see appendix)

$$[\text{Cl}^-]_t = [\text{Cl}^-]_\infty \left\{ 1 - e^{-\beta \cdot t} \right\} \quad (2)$$

where $[\text{Cl}^-]_\infty$ is the equilibrium concentration of chloride in the wash solution and β is an empirical constant dependent on temperature and the nature of the solid phase.

In conservation practice, the objects are not left in the same solution until the chloride concentration reaches equilibrium, instead the solutions are changed at regular intervals so as to maximise the rate of chloride removal or conversely to minimize the total treatment time. For this purpose the most useful parameter is the initial rate of chloride removal into a chloride free solution. Calling this value R it follows from equation (2) that

$$R = \left\{ \frac{\partial [\text{Cl}^-]}{\partial t} \right\}_{t=0} = \beta \cdot [\text{Cl}^-]_\infty \quad (3)$$

With all of the samples studied, the experimental rate of increase of chloride in the wash solution was found to follow equation 2. The values of β , $[\text{Cl}^-]_\infty$ and R for a number of sets of samples are collected in Table II.

Working from equation 1 the effects observed for pH and temperature changes (Table II) are readily explicable. An increase in pH (OH^- concentration) will push the equilibrium to the right and will increase the rate of the forward reactions. An increase in temperature speeds up both the forward and backward reactions and by approximately the same extent. The net effect of a temperature increase is to make the time required to approach equilibrium

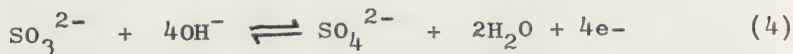
much shorter but not altering the equilibrium itself to any significant amount. By maximising both these factors, that is, using a high pH (e.g. 0.5 M NaOH) and a heated solution, a rapid and efficient release of chloride from the iron artifact should be achieved.

Technique for removal of chloride ions

Unfortunately, when a corroded iron object is placed in a hot caustic solution, a breakdown of the iron corrosion product occurs and a red flocculent precipitate is formed. If this process is allowed to continue the corroded regions become very soft and eventually break apart. The red material formed in the solution under these conditions appears to be hydrated hematite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). This may be present in the sample before treatment or it may be formed by the conversion of FeOCl (equation 1) or the corrosion of metallic iron particles (3).

The formation of hydrated hematite can be prevented by making the electrochemical potential of the iron more negative, so that magnetite (Fe_3O_4) becomes the thermodynamically favoured iron oxide. This potential can be achieved by either impressing an external negative potential on the iron object (electrolysis) or by adding a reducing agent to the alkaline solution (chemical reduction). The latter method, discussed below, requires much simpler equipment and it eliminates the danger of exfoliation of the outer corroded regions of cast iron objects due to hydrogen evolution from the metal surface. In addition, a chemical reduction method is preferred for those badly corroded iron objects where attachment of a current contact to the remaining metal core is difficult without damaging the object.

In considering which reducing agent to use, the factors which we took into account were, firstly, the ease of removal or neutralization of any excess reactants and products remaining in the objects after treatment and, secondly, the general availability and cost of the chemicals. On this basis the most satisfactory reducing agent seems to be sodium sulfite (Na_2SO_3). This chemical is widely used in the food preserving industry and consequently is readily available and fairly inexpensive. The half reaction for SO_3^{2-} oxidation in alkaline solutions is



Any excess reagent or product remaining in the corroded region after treatment can be fixed as the insoluble barium salts (BaSO_3 ; BaSO_4) by simply.

washing the object in a $\text{Ba}(\text{OH})_2$ solution.

When a marine iron object is washed in a hot solution containing 0.5 M NaOH and 0.5 M Na_2SO_3 it is found that the iron compounds are entirely converted to magnetite. Table III gives the results of an X-Ray analysis of an alkaline sulfite treated sample which initially contained no metallic iron in the corrosion region. The only compounds present in this sample after treatment are magnetite, quartz (SiO_2) and graphite, the latter does not appear in the X-Ray analysis due to its low atomic weight.

The reduction of the iron compounds to magnetite has two effects on the release of chloride from the sample. Firstly, magnetite, density 5.18gm/cm^3 , is more dense than hydrated hematite, density $2.44 - 3.60\text{gm/cm}^3$. Consequently the conversion of hydrated hematite to magnetite produces a decrease in the volume of the solid phase and a corresponding increase in the void space and porosity of the corroded region. The increased porosity will result in a faster exchange of soluble reactants and products, between the inner corrosion regions and the bulk solution. Secondly, the removal of hydrated hematite from the corroded regions reduces the tendency for chloride ions to substitute for hydroxy ions in the solid (the back reaction in equation 1). With this back reaction eliminated or rather suppressed, the kinetics of chloride release become almost independent of the chloride concentration in the liquid.

Figure 2 shows the rate of release of chloride from a partially corroded cannonball during treatment at 60°C in 0.5 M NaOH, 0.5 M Na_2SO_3 solution. In this experiment the solution was changed part way through thus reducing the concentration of chloride in the solution from 500ppm to 40ppm, but no change was observed in the rate of release of chloride from the solid. In the same Figure it is seen that after 48 days the release of chloride from the solid ceased abruptly, indicating that washing was completed. This is in contrast to the "trailing off" effect observed in solutions without the reducing agent (Figure 1).

If the concentration of chloride in the wash solution becomes sufficiently high (over approximately 500ppm) some absorption of chloride ions on the magnetite does occur and an equilibrium approach effect in the chloride release curve is again observed. This is less pronounced than with the hematite based corrosion products as magnetite is a much weaker chloride ion absorber. For example, samples of iron corrosion product recovered from the Batavia are found to contain between 0.1 to 0.4% chloride by weight

if the iron is present mainly as magnetite, and between 6 to 14% chloride if hydrated hematite; in both cases the corrosion products are presumably in equilibrium with the chlorides in the surrounding seawater.

The effectiveness of alkaline sulfite washing in the removal of chlorides from the corrosion products was determined by measuring the amount of chloride in the solid. Table IV shows a typical chloride concentration profile in a partially corroded cannonball before and after treatment. The fraction of the chlorides extracted from the solid varies somewhat from one object to another but it is always greater than 97%. Long term exposure tests, at present in progress, will determine if the chlorides remaining in the corrosion product after treatment have a deleterious effect on the stability of the artifact.

A disadvantage with washing in a sulfite solution, or indeed any solution containing a chemical reducing agent, is that the free entry of atmospheric oxygen into the system must be prevented. If this is not done the reducing agent will rapidly be exhausted in converting oxygen to hydroxyl ions. This problem can readily be overcome by carrying out the reduction in a sealed container. For this purpose we have found reuseable 200 litre drums to be quite satisfactory. Provided the drums are at least $\frac{3}{4}$ filled with solution, removal of entrapped atmospheric oxygen by nitrogen purging is not necessary.

Summary of Alkaline Sulfite Treatment Method

One hundred and fifty litres of 0.5 M Na_2SO_3 and 0.5 M NaOH are prepared in a reuseable 200 litre drum. Into this solution the objects to be treated are placed, the drum is sealed and then placed in a water bath at 70°C. Each week samples of the solution are withdrawn and the chloride content determined. When the chloride content becomes constant, the solution is replaced with fresh alkaline-sulfite solution. This is continued until no more chloride is released from the objects. The objects are then removed and washed, at room temperature, in successively, deionized water (twice), 0.1 M $\text{Ba}(\text{OH})_2$, deionized water, acetone and then allowed to dry. After drying the wrought iron objects are painted (4) and the cast iron objects wax impregnated (4).

Conclusion:

The alkaline sulfite washing method increases the hardness of the graphitized region of cast iron objects and gives excellent retention to any surface markings or inscriptions. The colouration produced, a dull matt black, is aesthetically satisfactory. In addition,

no mechanical stress is placed on the object hence even the most delicate articles will not suffer from this treatment. At the time of writing, long term tests are being carried out to determine if the degree of chloride removal achieved by this method is sufficient to impart permanent stability to the iron artifacts.

Acknowledgements:

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Appendix

For the reaction



the Rate of forward reaction = $k_1 \times (\text{Number of moles of FeOCl}) \times [\text{OH}^-]$

and Rate of backward reaction = $k_2 \times (\text{Number of moles of FeOOH}) \times [\text{Cl}^-]$

where k_1 and k_2 are the respective rate constants.

Letting $N\text{-FeOCl}$ represent the number of moles of FeOCl and V_1 the volume of the wash solution then

$$\text{Rate of chloride release for solid} = V_1 \cdot \frac{d[\text{Cl}^-]}{dt}$$

$$\text{and } V_1 \cdot \frac{d[\text{Cl}^-]}{dt} = k_1 \cdot N\text{-FeOCl} \cdot [\text{OH}^-] - k_2 \cdot N\text{-FeOOH} \cdot [\text{Cl}^-]$$

To simplify, we assume that $N\text{-FeOOH}$ remains approximately constant throughout the washing procedure, that is, initially there is much more FeOOH present in the sample than there is FeOCl; then at any time

$$N\text{-FeOCl} = N^0\text{-FeOCl} - V_1 \cdot [\text{Cl}^-]$$

where $N^0\text{-FeOCl}$ is the initial number of moles of FeOCl Present.

This gives

$$V_1 \cdot \frac{d[\text{Cl}^-]}{dt} = k_1 \cdot (N^0\text{-FeOCl} - V_1 \cdot [\text{Cl}^-]) [\text{OH}^-] - k_2 \cdot N\text{-FeOOH} \cdot [\text{Cl}^-]$$

$$\text{or } \frac{d[\text{Cl}^-]}{dt} = k_1 \cdot N^0\text{-FeOCl} \cdot [\text{OH}^-] - \left\{ k_1 \cdot [\text{OH}^-] + \frac{k_2 \cdot N\text{-FeOOH}}{V_1} \right\} \cdot [\text{Cl}^-]$$

Grouping into constants α and β this gives

$$\frac{d[\text{Cl}^-]}{dt} = \alpha - \beta \cdot [\text{Cl}^-]$$

and on integration

$$\ln \left\{ \frac{\alpha - \beta \cdot [\text{Cl}^-]_t}{\alpha} \right\} = -\beta \cdot T$$

at $T = \infty$; $[Cl^-]_{\infty} = \alpha / \beta$ hence
 on substituting and rearranging

$$[Cl^-]_t = [Cl^-]_{\infty} \cdot (1 - e^{-\beta \cdot T})$$

This derivation assumes a rapid exchange of solutes between the inner regions of the corrosion and the bulk solution giving homogeneous reactivity throughout the solid phase. When this requirement is not met, as, for example, with impervious corrosion products, deviations from this simple rate release equation can be expected.

Table I
X-Ray analysis of untreated cast iron corrosion product

Observed		α - FeO(OH)		δ - FeO(OH)		Fe		FeOCl		SiO ₂	
d	I	d	I	d	I	d	I	d	I	d	I
4.15	9	4.18 100								3.34	100
3.32	30					3.42	100				
2.54	26			2.55	100	2.53	84			2.46	12
2.44	26							2.36	42		
2.37	26			2.26	100					2.28	13
2.28	13										
2.10	22							2.05	10		
2.06	13										
2.02	22										
2.00	100					2.01	100				
1.97	17										
1.86	26							1.89	42		
1.85	17							1.81	30	1.82	17
1.68	17			1.69	100						
1.64	13							1.64	30		
1.51	9							1.52	40	1.54	15

Table II

Parameters for chloride concentration in wash solutions of
marine iron corrosion products (Equations 2 and 3)

Set	No.	pH	Temp (°C)	(Cl ⁻) ppm	β days ⁻¹	R (ppm/day)
A	1	8.3	30	800	0.130	105
	2	13.4	30	3,300	0.119	395
B	1	4.8	30	1,040	0.109	110
	2	10.3	30	4,800	0.048	230
C	1	8.3	30	670	0.107	70
	2	12.1	30	1,800	0.061	110
D	1	13.4	15	1,180	0.548	650
	2	13.4	40	1,290	1.404	1810
	3	13.4	60	1,350	2.270	3100

All samples are wrought iron except set D which is cast iron.

Table III
X-Ray analysis of alkaline sulfite treated cast iron corrosion product

Observed		Fe_3O_4		SiO_2	
d	I	d	I	d	I
3.33	M			3.34	100
2.96	M	2.96	70		
2.52	VS	2.53	100		
2.09	M	2.09	70		
1.61	W	1.61	85		
1.49	S	1.48	85		

Table IV

Concentration of chlorides (ppm) in corrosion product of cannonball before and after alkaline sulfite treatment (solid metal at 29mm below original surface)

Depth (mm)	0 - 4	4 - 8	8 - 12	12 - 16	16 - 20	20 - 24	24 - 28
Before	6,000	117,000	85,000	90,000	75,000	69,000	121,000
After	7	5	31	51	150	740	1,200

Figure 1

75/13/3-13

Concentration of Chloride in Wash Solution (ppm)

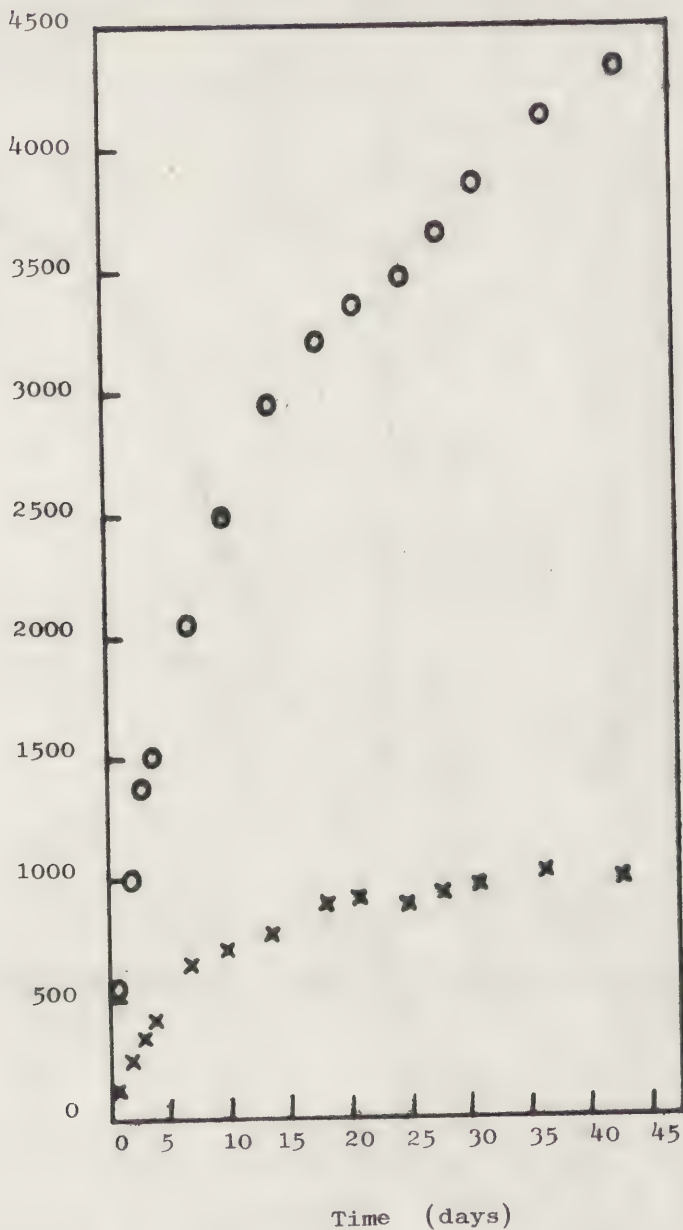


Figure 1 Concentration of chloride in wash solutions of two matched solid samples; O - at pH of 12.1 and X at pH of 4.8

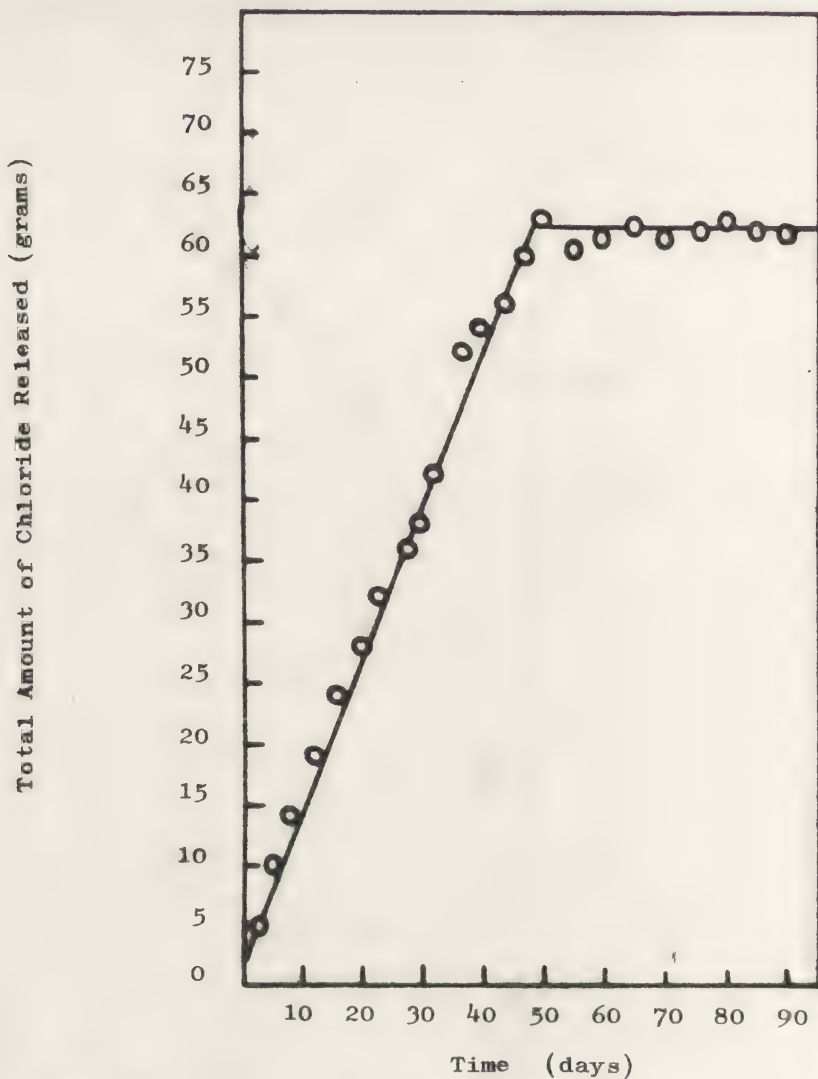


Figure 2
Release of chloride from a partially corroded
cannonball washed in alkaline sulfite solution
at 60°C

LEGISLATION FOR THE PROTECTION OF SHIPWRECKS IN WESTERN AUSTRALIA

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Abstract

In Western Australia, legislation to protect the numerous shipwrecks lying off the coast was first passed in 1964. This has since been twice revised and now exists as the Maritime Archaeology Act 1973, which vests these wrecks in the Western Australian Museum. This paper discusses the principles of the Act and its mode of operation, but concludes with the proposal that the most effective means of exercising this responsibility is to carry out an active wreck excavation and inspection programme, backed by adequate conservation and restoration facilities.

Introduction

In Western Australia, State legislation exists to preserve, on behalf of the community, the remains of ships and associated relics lost before the year 1900. To date this includes four Dutch East Indiamen wrecks (Batavia 1629, Vergulde Draeck 1656, Zuytdorp 1712 and Zeewijk 1727), an English wreck (Tryal 1622) and in excess of 1000 colonial wrecks which is surprisingly high considering that Western Australia was not colonised until 1829.

Legislation was first introduced in 1964 (Museum Act 1959-64) because some of the wrecks were being looted, to recover silver bullion, resulting in extensive damage to the sites. This legislation was revised in 1969 (Museum Act 1969) and finally in 1973 proclaimed as an independent act - the Maritime Archaeology Act 1973 (1). By this Act the property and right to possession of all historic ships (i.e. those lost before the year 1900) and maritime archaeological sites are vested in the Western Australian Museum on behalf of the Crown.

Maritime Archaeological Sites

The Act is designed to protect not only the relics on a wreck site but also those removed from the site including the remains of survivors, jettison, in fact anything of historic interest which was associated with an historic ship. For this reason the wreck of an historic ship is known as a maritime archaeological site and may be situated under water or on land, and can be defined as:

1. any area in which the remains of a ship, which in the opinion of the Director of the Museum may have been an historic ship, are known to be located;
2. any area in which any relic is known to be located, or where in the opinion of the Director unrecovered relics associated with a ship which may have been an historic ship are likely to be located; and
3. any structure, campsite, fortification or other location of historic interest that, in the opinion of the Director, is associated with, and was occupied or used by, persons presumed to have been in an historic ship.

Protected Zones

For the purpose of preventing plunder or damage to a maritime archaeological site the area surrounding the site can be declared a protected zone and may include the waters lying above the site, the sea bed below it, or land. The information regarding the protected zone, including its boundaries, must be published in the Western Australian Government Gazette which then makes it possible to restrict access to the zone to prevent the entry of boats, diving on the site or the use of diving equipment and excavation tools including underwater explosives.

Reporting New Finds

Any person who finds what appears to be an historic ship must notify the Director of the Western Australian Museum. If it turns out that it is an historic ship or an associated relic the position of which was not previously known, then the finder may be eligible for a reward. In order to qualify for the reward the finder must:

1. state the time and date of the finding
2. submit a description of the ship or relic and of any distinguishing features sufficiently detailed to ensure so far as is practicable that it may subsequently be positively identified

3. give particulars of any buoy or other thing by which the claimant has marked the position
4. give as accurate description as is practicable of the position
5. set out the particulars of the finder and the circumstances in which the find was made, including particulars of any other persons present or who rendered assistance.

If the finder is dissatisfied with the decision of the Trustees of the Museum concerning a reward then he can appeal to a Judge in chambers.

If the new find is identified as an historic ship or associated relic then it automatically comes under the provisions of the Act. However, where it is decided that it is not of national or local historical interest or of scientific, archaeological, educational or other special national or local interest, then the provisions of the Act no longer apply. In this case the information is published in the Government Gazette so that persons are aware that they are not liable for prosecution if they dive on or recover relics from that site.

Disposal of Material

In order to ensure that the maritime archaeological collections are not broken and dispersed, the Act gives the Trustees of the Museum control over the disposal of the recovered material. When they are satisfied that any relic has been preserved, examined and recorded they can recommend that the relic should be disposed of to

1. the Commonwealth of Australia, or any State or Territory of the Commonwealth, the body known as The National Trust of Australia (W.A.), or the body known as the Royal Western Australian Historical Society Incorporated;
2. a person or body having historic associations with that relic; or
3. the finder, or a person who recovered or assisted in the recovery of, the relic.

Offences Against the Act

A person who violates the Act in any way may be prosecuted, and the penalties, depending on the offence, can be two thousand dollars or imprisonment for twelve months or both the fine and imprisonment. There is also provision in the Act for the confiscation of vessels, vehicles or equipment involved in illegal operations in a protected zone.

Netherlands-Australia Agreement on VOC Wrecks

Due to various challenges to the validity of the early legislation, another means of protecting the wrecks has been achieved by the Netherlands Government, as the legal successor to the Dutch East India Company (VOC), transferring to the Australian Government their title to the VOC wrecks lying off the coast of Western Australia.

The Deed of Transfer and Agreement between the Netherlands and Australia concerning old Dutch Shipwrecks has been signed and will operate under the following principles:

1. The Netherlands will transfer to the Australian Commonwealth all its right, title and interest in and to the wrecks of former vessels of the VOC lying on or off the coast of Western Australia, and in and to any articles recovered from the wrecks including articles already recovered and in possession of the State of Western Australia and its authorities and also articles recovered before the Museum Act.
2. The historic wrecks are the national heritage of both Netherlands and Australia. Therefore a committee comprising two persons nominated by the Commonwealth and two by the Netherlands will be set up to determine the disposition and subsequent ownership of articles recovered from the wrecks.
3. As the cost of recovery of the articles far exceeds their intrinsic or antiquarian value then this expenditure can only be justified on the basis of the historic importance of the material. This means firstly that a representative collection of the wreck material should be deposited in the Museums of both The Netherlands and Australia and secondly, which is of more importance, that the material should not be dispersed to the point where historians are not able to reassemble and study the material when necessary. Therefore strict control of the secondary distribution within The Netherlands and Australia is essential. The bulk of the material will in fact be held in the Western Australian Museum. The institutions receiving material will be expected to contract not to disperse it further and to agree to allow its reassembly for study.

Operation of the Act

Although the Maritime Archaeology Act and the Agreement on VOC wrecks between the Netherlands and Australia make it legally possible to protect historic ships, this is difficult in practice. Blasting and looting of the Vergulde Draeck and also the Tryal have occurred since

the passing of the earlier legislation and although several prosecutions have been initiated, to date no convictions have been obtained. It is hoped that the new Act will overcome some of the problems found with the earlier legislation.

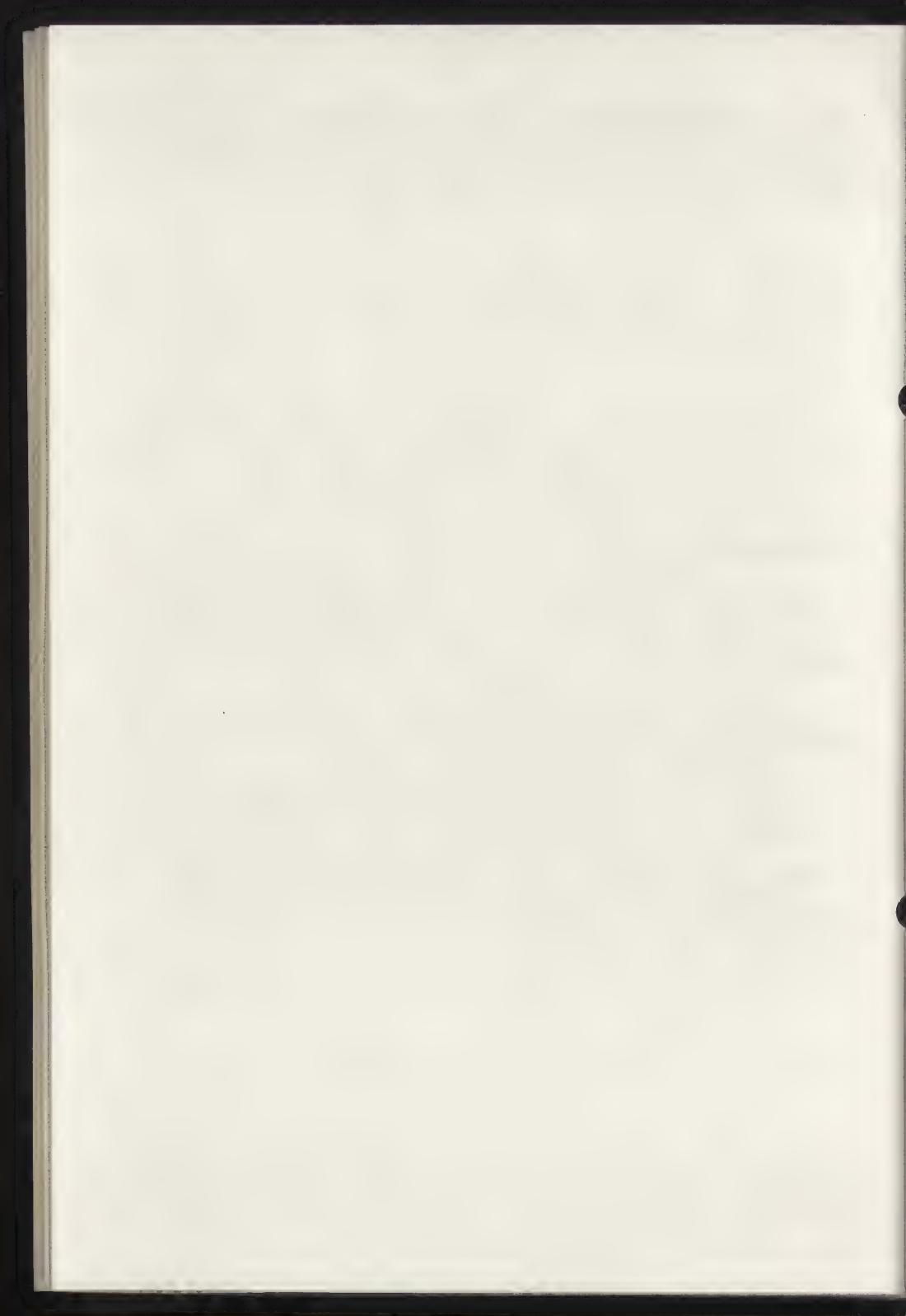
The Museum has found that the best method of operating under the Act is to carry out an extensive wreck excavation (2) and inspection programme using its own personnel. It now has a very well staffed and equipped Department of Maritime Archaeology backed by a Conservation Laboratory specialising in marine archaeological material (3). In addition it uses the assistance of local skin-diving clubs. The necessity for good public relations between the Museum and these clubs cannot be overstressed as club members are most likely to find new wrecks, and have opportunities to remove material from existing known wrecks. Co-operation is achieved most successfully through the organisation of combined diving expeditions.

Statement by Author

This paper is based on my personal interpretation of the Western Australian Government Maritime Archaeology Act, 1973. Any person wishing to consult the details of the Act is advised to refer to the full publication (1).

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2. Green, J.N. (1973). The wreck of the Dutch East Indiaman the Vergulde Draeck, 1656. Int. J. Naut. Archaeol. and Underwater Archaeol. 2, 267-289.
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PROCÉDÉS MÉCANISÉS: LE SYSTÈME VINYECTOR

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Parmi les différents objets que recouvre le concept de biens culturels, il est évident que ceux dont le nombre a le plus augmenté ces derniers temps sont ceux destinés aux archives et aux bibliothèques, à savoir les documents graphiques.

Il est superflu de souligner l'utilité et l'importance du document graphique ainsi que les multiples facteurs de dégradation qui atteignent sa faible nature physique. Par contre, il est urgent de revoir, sans cesse et en profondeur, tous les moyens et procédés à notre portée pour faire face et remédier à la situation de milliers et de milliers de livres et de documents atteints ou menacés d'une détérioration qui découle de leur nature même ou de leur milieu environnant.

Il faut se convaincre de ce que la restauration ne peut jamais remplacer ce que n'obtient pas la préservation. La restauration doit exclusivement intervenir quand la dégradation a dépassé le stade de la prévention. Même ainsi, l'équilibre entre les dégâts et les possibilités de récupération est presque hors d'atteinte.

L'augmentation spectaculaire de la masse des documents graphiques est due au rendement remarquable des systèmes mécanisés qui ont transformé en progression logarithmique le rythme arithmétique de la production manuelle.

Cette augmentation a entraîné proportionnellement celle du matériel à garder. Les difficultés de conservation sont plus grandes, de même que la menace de décomposition physique, conséquence de la dégradation de la qualité, liée à la production de masse.

Il est donc nécessaire que la révolution des techniques de papeterie et d'impression se reflète dans les moyens et procédés qui, aussi bien dans le domaine préventif que curatif, garantissent la pérennité des documents graphiques.

Face à ce problème et sans oublier les tentatives visant à améliorer la qualité des papiers et des encres, qui, malheureusement, ne parviennent pas à vaincre ou à compenser les intérêts commerciaux, et face à des difficultés qui dépassent nos objectifs actuels, nous avons envisagé la situation du point de vue qui nous concerne le plus : la restauration.

Sous cet aspect, il faut reconnaître que les résultats obtenus, bien qu'encourageants, sont encore loin d'une réalité actualisée.

Une fois au-delà de la longue étape expérimentale, les présents efforts de recherche doivent déboucher sur une nouvelle technicité permettant de comparer les méthodes d'obtention et les systèmes de restauration. Autrement, l'écart entre les documents exigeant un traitement approprié et les possibilités de restauration pourra s'agrandir encore davantage.

Conscients du problème, nous pouvons, de façon générale, classer les documents graphiques en deux grands groupes, selon leur nature :

a) le document singularisé, qui a les caractéristiques de l'exemplaire unique, où l'unité est le tout et qui peut très bien se comparer à l'oeuvre d'art ;

b) le livre, le dossier, le regroupement de plusieurs documents formant une même unité de volume, conçus et matérialisés par des traits communs.

Il va de soi que la restauration doit distinguer entre les deux cas. La main patiente qui a exécuté l'oeuvre unique ne peut être remplacée que par une autre main analogue. Mais l'artisanat ne peut pas concurrencer une technicité actualisée. Délimitons donc bien les deux champs, qui doivent être parallèles, ce qui, au besoin, n'exclut pas les convergences logiques. Réserveons d'un côté le travail manuel, artisanal, à ce qui a été créé de la sorte, mais appliquons de l'autre les techniques modernes aux documents qui ont eu la machine pour berceau.

Nous insistons sur le fait que sinon le déséquilibre s'accroîtra progressivement autant que les limites des possibilités humaines face à la machine que l'homme lui-même a su créer pour sa commodité.

Dans cette optique, le Service espagnol de Restauration des Livres et des Documents a dressé le bilan de ses ressources et a voulu

accroître son rendement, sans oublier à aucun moment les règles de la préservation et de la restauration, qui peuvent se résumer par l'axiome médical: "primum non nocere", signifiant qu'il faut avant tout ne pas causer davantage de tort.

Il a été fait dans ce but une analyse minutieuse des différents moyens et procédés qui interviennent dans le processus de restauration le plus généralisé, à savoir: stérilisation, lavage, élimination des taches, blanchiment, neutralisation, réintégration des parties perdues, séchage et repassage.

Il a été constaté qu'en cours de traitement, le document subissait une série de rétentions, de manipulations, de passages d'un bain à l'autre... s'accompagnant d'une grande consommation de produits, qui n'étaient pas toujours récupérables, et qu'il était exposé à divers risques résultant des déplacements, des interruptions du processus et de l'existence obligatoire de différents instruments et zones de travail.

Nous avons par conséquent envisagé la possibilité de renverser la situation. La solution consistait à garder le document en un seul endroit centralisant tous les traitements, au lieu que ce soit le document qui se déplace en fonction des exigences du processus.

Le fruit de nos recherches a été la conception et la construction (1) d'un ensemble de deux machines complémentaires qui réalisent dans sa totalité le processus mentionné ci-dessus, en obtenant non seulement la continuité du traitement, mais aussi un rendement supérieur et une finition de meilleure qualité.

(1) L'auteur du présent rapport avait annoncé la conception d'un premier modèle de cette machine lors du congrès de l'IIC qui a eu lieu à Lisbonne en 1972.

De même, un exposé sur le second modèle a été fait lors du 11e Séminaire organisé par "The Library of Athenaeum" de Boston. Cet exposé a été publié dans le numéro 133-4, pp. 187-194, de la "Revista de la Dirección General de Archivos y Bibliotecas", Madrid, 1974.

Cette même année a vu la fabrication d'un troisième modèle entièrement automatisé.

Comme il a été indiqué, le système, baptisé "Vinyector", se compose de deux machines complémentaires.

La première dispose d'un châssis mobile sur lequel on met le ou les documents. Une fois introduit dans la machine et sans cesser d'être observé, le document peut être traité indistinctement au moyen d'un gaz ou d'une solution aqueuse. Un automatisme de transvasement permet d'appliquer l'élément souhaité qui ensuite, s'il s'agit d'un gaz, peut être expulsé à l'extérieur, ou dans le cas de liquides, retourner, à travers un filtre, dans son récipient, où il attend une nouvelle possibilité d'emploi.

Pour restaurer le document dans son intégrité, la machine utilise de la pâte à papier qui, logiquement, n'est pas restituable puisque le but est de remplacer les parties manquantes du document. Pour les autres opérations, elle emploie n'importe lequel des produits actuellement utilisés.

Le rendement obtenu est surprenant. Tandis qu'avec le système manuel classique, on traitait une feuille, avec le système en question, pour un temps et des moyens analogues, il a toujours été obtenu des proportions de rentabilité supérieures au rapport 1:100.

Les avantages de ce résultat sont accrus par la limitation de l'espace occupé et des appareils employés, l'élimination des risques, l'unité des résultats, la possibilité de réutiliser les produits, etc. En outre, ce qui est plus important à notre avis, il est désormais possible de s'occuper, avec toute garantie, en un temps et avec un personnel réduits, du traitement des pièces qui, vu leur état avancé de dégradation, étaient toujours laissées de côté pour plus tard, pour des raisons soit techniques, soit humaines.

Cette productivité a toutefois été à l'origine d'un nouveau problème: l'accumulation de documents traités dans les sècheurs et dans les presses. Afin de remédier à cet inconvénient, le système a été complété avec la seconde machine qui réalise simultanément le séchage et le repassage. On y installe le même châssis, qui contient le document traité dans la première machine. En combinant et en contrôlant la température et le vide, on obtient une finition parfaite en un laps de temps très court.

Avec ce procédé, nous avons pu mener à bien la restauration de livres et de dossiers qui attendaient en vain d'être traités, en plus d'entrevoir la possibilité de réduire le volume des documents encore en souffrance.

En conclusion, j'insiste sur les exigences particulières de certaines oeuvres qui doivent être traitées suivant des processus adaptés à chaque cas. Mais devant la masse non moins précieuse des documents qui s'accumulent à l'heure actuelle, il est inacceptable de reporter davantage l'adoption de mesures conformes aux exigences des temps nouveaux. Il est indéniable que de nos jours, la mécanisation fournit l'espoir le plus sûr d'atteindre l'objectif qui, en définitive, est le nôtre.

Résumé

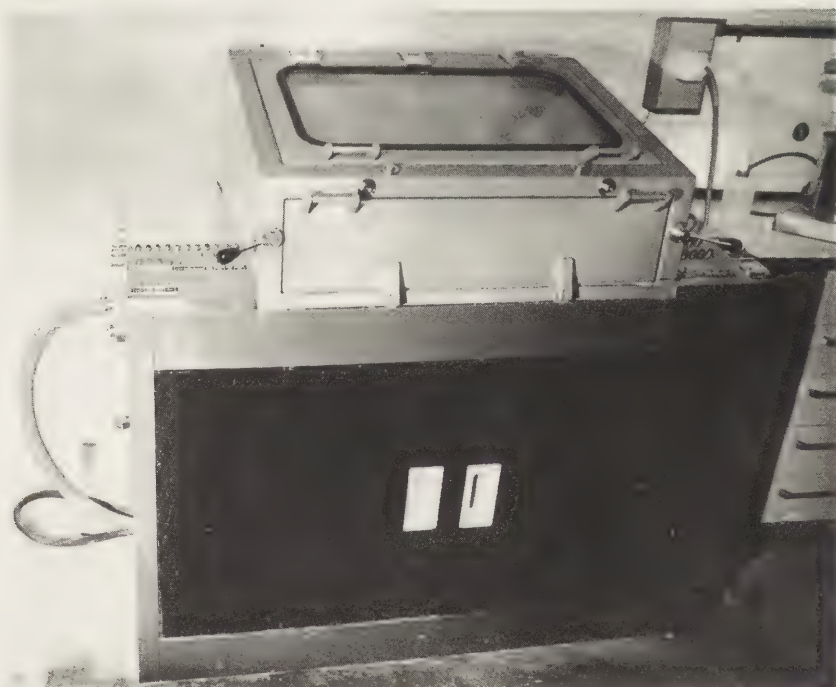
L'accroissement vertigineux de la quantité de documents graphiques - grâce aux possibilités offertes par les procédés industriels répondant à un besoin socio-économico-culturel - aboutit à un double problème: conservation de documents fragiles par nature et disproportion grandissante entre les documents attendant d'être restaurés et les possibilités de traitement.

Alors qu'aujourd'hui, le document graphique a la machine pour berceau, la restauration recourt toujours à des procédés manuels classiques.

Il faut dès lors, de toute urgence, réduire ces écarts alarmants en introduisant de nouveaux procédés qui allégeront les tâches de restauration.

A l'issue d'une phase expérimentale, le Service espagnol de Restauration des Livres et des Documents a conçu et construit un système mécanique de restauration dont les rendements dépassent la proportion de 1:100 par rapport aux systèmes manuels.

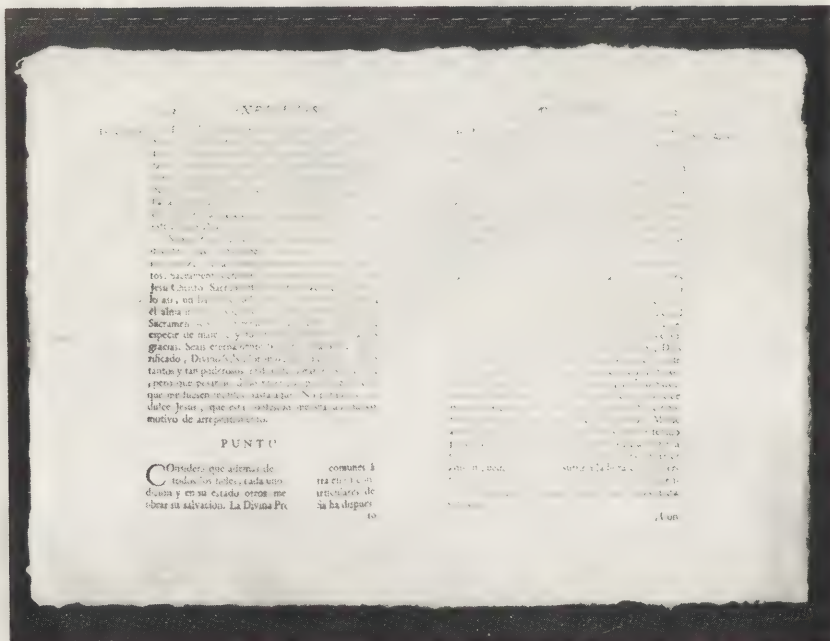
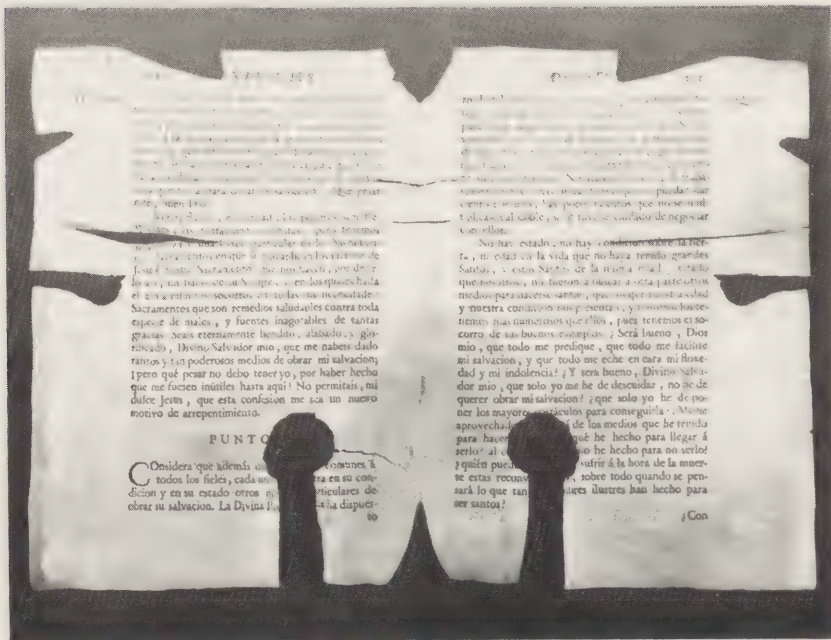
Le système, appelé Vinyector, utilise les moyens gazeux ou aqueux actuels en éliminant les aspects négatifs et en améliorant la qualité des résultats.



1.- Modèle Vinvector II (maniable)
2.- Modèle Vinvector III (automatique)



3.- Vue partielle du laboratoire.
4.- Préparation du document à traiter.



5.- Document avant être traité.
6.- Document après le traitement.

LA LAMINATION DES PAPIERS

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La lamination des documents a pour effet de renforcer les vieux papiers devenus cassants et donc très difficilement manipulables. Dans ce procédé, on dispose le document altéré entre deux pellicules plastiques et deux épaisseurs de tissu ou papier transparent et très fin ; on fait adhérer l'ensemble par fusion ou dissolution du film plastique. Dans certains cas, on consolide le document uniquement avec la pellicule plastique, sans utiliser de "tissu de renforcement" ; il s'agit alors d'une imprégnation.

Deux rapports concernant ce problème ont déjà été présentés par le Dr WERNER* lors de réunions précédentes du Comité de Conservation de l'I.C.O.M.

En 1965, le Dr WERNER faisait une longue énumération de toutes ces techniques. Cette liste est toujours valable mais on doit cependant y adjoindre de nouvelles méthodes employées depuis lors.

En 1967, le même auteur exposait les résultats de l'étude que nous avons réalisée en collaboration sur trois méthodes de lamination : méthode Barrow, méthode indienne et méthode Postlip. Les conclusions de ce travail étaient difficiles à dégager, les résultats obtenus par les deux laboratoires étant très disparates. Il fut donc décidé de poursuivre les expériences.

Le but du travail que nous résumons ici est d'étudier le comportement de plusieurs papiers laminés, non seulement par les techniques que nous avons analysées en 1967, mais également par celles utilisées actuellement dans les différents ateliers mondiaux. Ces méthodes étant extrêmement nombreuses et variées, il ne nous a pas encore été possible de toutes les expérimenter. Nous en avons pour l'instant sélectionné 16 se répartissant en plusieurs groupes, en fonction du film plastique employé : acétate de cellulose, acétate de polyvinyle, polyamide et polyéthylène.

* The lamination of documents, I.C.O.M., Washington, 1965, multigr.

A study of lamination techniques (en collaboration avec Mme FLIEDER), I.C.O.M., Bruxelles, 1967, multigr.

Afin de s'assurer de l'innocuité des techniques de lamination vis-à-vis du support, nous avons traité deux papiers de qualité différente par toutes les méthodes sélectionnées. Leur résistance physico-chimique a été examinée avant et après lamination, ainsi qu'après un cycle de vieillissement artificiel. Toute restauration devant être réversible, le comportement des papiers une fois la lamination retirée a été également analysé *.

Nous avons travaillé avec un papier AFNOR VII/1 (100 % pâte chimique blanchie) et un papier AFNOR VII/5 (100% coton et traces pâte chimique blanchie). Toutes les mesures de résistance mécanique et chimique ont été réalisées selon les normes AFNOR ** :

résistance à la plière, à la traction, à l'éclatement, à la déchirure, mesure de blancheur, d'opacité et du pH. Nous avons étudié le degré d'oxydation et de polymérisation de la cellulose uniquement pour les papiers délamés. Le poids et l'épaisseur des documents d'archives étant deux facteurs très importants pour le conservateur, nous avons systématiquement effectué des mesures de grammage et d'épaisseur des papiers laminés.

Le vieillissement artificiel retenu est de 4 jours dans une étuve sèche ventilée maintenue à 80°C.

La résistance du papier laminé et délamé a été comparée avec celle du papier témoin et la résistance du papier laminé vieilli et délamé vieilli avec celle du papier témoin également vieilli.

RESULTATS EXPERIMENTAUX

1. ACETATE DE CELLULOSE : qu'il s'agisse d'une lamination à chaud ou à froid, ou d'imprégnation, l'aspect du document traité ainsi que sa lisibilité sont bons. Le papier laminé est néanmoins assez rigide.

1.1. Lamination à chaud "Barrow" (tableau et graphique 1) : la résistance mécanique et chimique des deux papiers laminés est bonne, ce qui confirme les résultats déjà obtenus en 1967 ; cependant on signale une légère perte de la résistance au double pli de l'AFNOR VII/1. Le pH a augmenté. On note un léger jaunissement.

* La délamination s'effectue en trempant les papiers laminés dans des cuvettes contenant les solvants appropriés. La plus grande partie du film ayant été retirée, on termine l'opération dans un soxhlet contenant 20 litres de solvant.

** NF Q 03.001, 03.011, 03.004, 03.014,
NF T 12.002, 12.004, 12.005

1.2. Imprégnation à chaud : la délamination est ici tout à fait impossible. Pour les deux papiers, la résistance au double pli et à la déchirure a très nettement diminué, tandis que les autres constantes mécaniques ne se sont pas modifiées. Les papiers laminés ont légèrement jauni ; après vieillissement ils se sont un peu acidifiés.

1.3. Lamination à froid "indienne" (tableau et graphique 2) : la perte importante de la résistance au double pli de l'AFNOR VII/1 signalée en 1967 n'a pas été confirmée ; nous notons au contraire, comme le Dr WERNER le signalait, une très nette augmentation de cette constante. Dans l'ensemble, la résistance mécanique des papiers laminés est excellente ; le pH a augmenté, les papiers ont légèrement jauni. Notons une perte assez importante de l'indice de Cu de l'AFNOR VII/5 délaminé vieilli.

2. ACETATE DE POLYVINYLE : l'aspect du document et sa lisibilité sont bons, mais les papiers laminés sont très rigides et semblent même parfois cassants.

2.1. Lamination "Langwell" (tableau et graphique 3) : dans l'ensemble, peu de modifications de la résistance physico-chimique des deux papiers laminés, en dehors d'une augmentation très sensible de la résistance au double pli et à la rupture de l'AFNOR VII/5 laminé et laminé vieilli ; le pH a augmenté et la blancheur ne s'est pas modifiée.

2.2. Lamination "Langwell" : les résultats sont très analogues à ceux obtenus avec la méthode précédente.

2.3. Area : le tissu de renforcement a très mal adhéré : le papier s'est dédoublé au moment des essais. Nous n'avons donc pas pu analyser les papiers ainsi traités.

3. POLYAMIDE : l'aspect esthétique du document et sa lisibilité sont excellents. On note une très grande souplesse du papier laminé, jamais observée jusqu'alors avec aucune autre méthode.

Quel que soit le procédé utilisé : Promatco (3.1.) ou Cerex (3.2.) (tableau et graphique 4), les résistances mécaniques des papiers traités sont exceptionnellement bonnes. La résistance à l'éclatement et à la pliure du polyamide, même après vieillissement, étant très élevée, il nous a été parfois impossible de mesurer ces constantes. Le pH a considérablement augmenté et la blancheur ne s'est absolument pas modifiée.

4. POLYETHYLENE : tous les documents traités sont très souples et la lisibilité très bonne. Malheureusement, les papiers laminés ont un aspect au toucher un peu "gras". Qu'il s'agisse de lamination ou d'imprégnation, la délamination est pratiquement impossible à réaliser, tout au moins si l'on désire retirer totalement le film de polyéthylène.

4.1. Lamination "Archives de Florence" (tableau et graphique 5) : la résistance mécanique du document est excellente spécialement pour la résistance à la pliure et à la déchirure. Le pH n'est pas modifié mais la blancheur a diminué.

4.2.-4.3. Lamination "Archives de Zagreb" : quel que soit le papier japon utilisé, la résistance mécanique des papiers laminés est bonne (légèrement inférieure à celle des papiers traités par les Archives de Florence). On note cependant que la désacidification n'a pratiquement pas d'effet. La blancheur a diminué plus fortement avec la méthode 4.2. qu'avec la méthode 4.3.

4.4. Imprégnation "Archives de Zagreb" : on note de très grosses pertes de la résistance à la rupture et à l'éclatement. La désacidification ici encore a peu d'influence. La blancheur a très légèrement diminué.

4.5. Imprégnation "Archives de Belgrade" (tableau et graphique 6) : il est important de signaler que le papier AFNOR VII/1 a pu être totalement délaminé. Néanmoins, comme dans le cas précédent, on observe une grande perte de la résistance à la rupture et à l'éclatement. Aucune modification du pH et de la blancheur.

CONCLUSION

L'ensemble de ces résultats nous montre que :

- Toutes les techniques d'imprégnation diminuent la résistance mécanique des papiers traités (qu'il s'agisse d'acétate de cellulose ou de polyéthylène). La délamination a presque toujours été impossible à effectuer. Il est donc souhaitable d'éliminer ce procédé.
- Le procédé classique à l'acétate de cellulose nous paraît être une très bonne solution. Cependant, on note une légère supériorité de la méthode indienne. Celle-ci a l'avantage d'être d'utilisation très aisée, peu onéreuse, mais assez toxique pour les restaurateurs s'ils n'opèrent pas dans un local extrêmement bien ventilé.
- Le papier japon imprégné d'acétate de polyvinyle semble donner de bons résultats. Il faut signaler néanmoins que le procédé "Langwell" réalisé en France peut entraîner dans certains cas une fragilité à la pliure.
- Le polyamide confère au document, non seulement une très grande souplesse, mais une résistance exceptionnelle à la déchirure et à la pliure. Ce procédé nous paraît être le meilleur parmi ceux que nous venons d'examiner. Les produits Promatco sont assez onéreux, le Cerex et le Bifix par contre sont d'un prix tout à fait abordable.
- Le polyéthylène donne une très bonne résistance mécanique au papier traité, mais malheureusement ce produit étant très difficile à solubiliser, la lamination n'est alors plus réversible. Dans ces conditions, on n'utilisera le polyéthylène que dans des cas très particuliers.

Ce travail est loin d'être achevé, car un très grand nombre de techniques et de produits doivent encore être expérimentés. Nous pensons également étendre nos investigations à l'étude du comportement au vieillissement de films plastiques et de tissus de renforcement ainsi qu'à l'étude de l'interpénétration des matériaux plastiques dans les fibres du papier, ceci en fonction de la température, de la pression et du temps de chauffage utilisés.

Centre de Recherches sur la
Conservation des Documents graphiques
Paris

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RESUME

La lamination des documents a pour effet de renforcer les vieux papiers devenus cassants et donc très difficilement manipulables. Nous présentons dans ce travail les résultats obtenus sur deux sortes de papiers laminés par 16 méthodes différentes se répartissant en plusieurs groupes en fonction du film plastique employé : acétate de cellulose, acétate de polyvinyle, polyamide et polyéthylène. La résistance physico-chimique des papiers laminés et dé laminés a été examinée avant et après vieillissement. Toutes les mesures ont été faites selon les normes AFNOR.

Nous avons constaté que les procédés d'imprégnation sont à éliminer et que les laminations au polyéthylène sont presque toujours irréversibles. Les techniques qui nous semblent les plus appropriées sont celles utilisant un adhésif et un "tissu de renforcement" en polyamide. Nous comptons poursuivre ce travail par l'étude d'un très grand nombre d'autres méthodes.

A N N E X E

DESCRIPTIF DES DIFFERENTES TECHNIQUES DE LAMINATION

1. ACETATE DE CELLULOSE - Délamination à l'acétone

1.1. Lamination à chaud "Barrow" (Archives Nationales - Paris)

Désacidification : bicarbonate de magnésium

Adhésif : film d'acétate de cellulose Acetophane 25 H incolore (Sté de Chimie et d'Entreprise - France)

Tissu de renforcement : papier japon

Laminator 140°C, 25 secondes

1.2. Imprégnation à chaud (Archives de Florence)

Adhésif : acétate de cellulose Moviphan

Tissu de renforcement : aucun

Presse chauffante 90°C

1.3. Lamination à froid "indienne" (Archives Nationales - Paris)

Désacidification : bicarbonate de magnésium

Adhésif : film d'acétate de cellulose Acetophane 25 H incolore (Sté de Chimie et d'Entreprise - France)

Tissu de renforcement : papier japon

Dissolution de l'acétate de cellulose avec rouleau imbibé d'acétone

2. ACETATE DE POLYVINYLE - Délamination à l'alcool éthylique

2.1. Lamination "Langwell" (Public Record Office - Londres)

Désacidification : acétate de magnésium

Tissu de renforcement : papier japon pré-imprégné d'acétate de polyvinyle vendu par les Ets ADEMCO (Grande-Bretagne)

Presse chauffante

2.2. Lamination "Langwell" (Archives Nationales - Paris)

Désacidification : bicarbonate de magnésium

Tissu de renforcement : papier japon imprégné d'acétate de polyvinyle (Lamatec vendu par ADEMCO - Gde Bretagne)

Laminator 80°C, 20 secondes

2.3. Area (Public Record Office - Londres)

Adhésif : solution d'acétate de polyvinyle (Vynamul 6815)

Tissu de renforcement : nylon 6815, ICI, Grande-Bretagne

Presse chauffante

3. POLYAMIDE - Délamination à l'alcool éthylique à 40°C

3.1. Promatco (Archives Nationales - Paris)

Désacidification : bicarbonate de magnésium

Adhésif : résille de polyamide Process nylon laminating tissue (Promatco - U.S.A.)

Tissu de renforcement : résille de polyamide Heat Set tissue acid free (Promatco - U.S.A.)

Laminator 80°C, 20 secondes

3.2. Cerex (Archives Nationales - Paris)

Désacidification : borax 1 %

Adhésif : résille polyamide Bifix (Lainières de Picardie - France)

Tissu de renforcement : résille polyamide Cerex (Monsanto - Grande-Bretagne)

Laminator 80°C, 20 secondes

4. POLYETHYLENE - Possibilité éventuelle de délamination avec du décalène à 80°C

4.1. Lamination "Archives de Florence"

Adhésif : film de polyéthylène "Polien"

Tissu de renforcement : papier japon

Presse chauffante 150°C

4.2. Lamination "Archives de Zagreb"

Avec ou sans désacidification (technique non communiquée)

Adhésif : film de polyéthylène

Tissu de renforcement : papier japon "Kuranai natur"

Presse chauffante

4.3. Lamination "Archives de Zagreb"

Avec ou sans désacidification (technique non communiquée)

Adhésif : film de polyéthylène

Tissu de renforcement : papier japon "Japico Langfaser
seiden Papier"

Presse chauffante

4.4. Imprégnation "Archives de Zagreb"

Avec ou sans désacidification (technique non communiquée)

Adhésif : film de polyéthylène

Tissu de renforcement : aucun

Presse chauffante

4.5. Imprégnation "Archives de Belgrade"

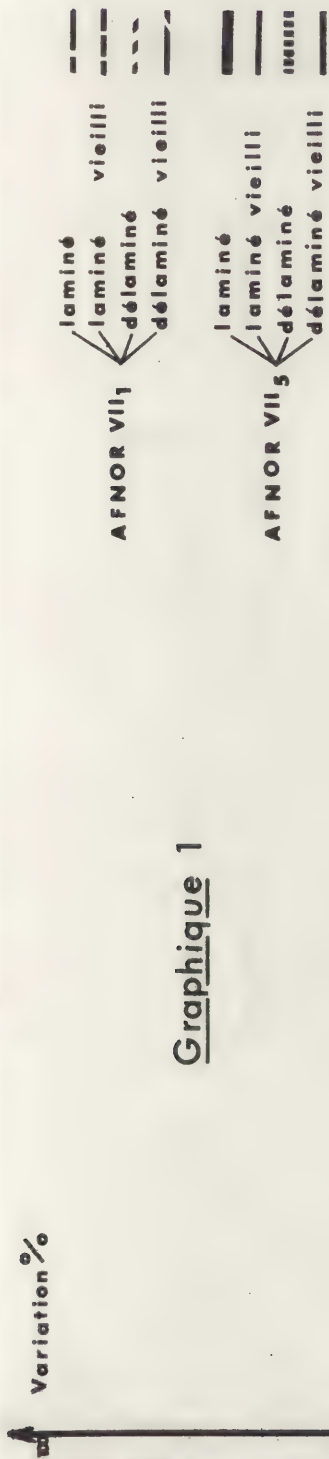
Adhésif : film de polyéthylène

Tissu de renforcement : aucun

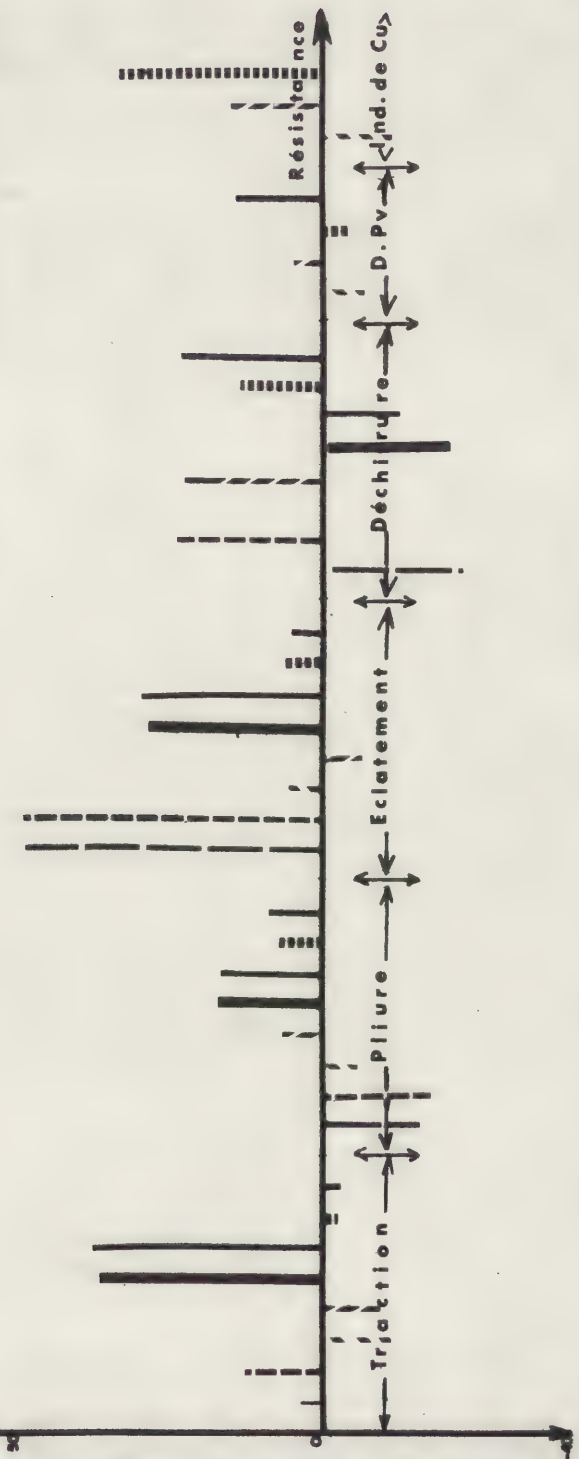
Impregnator 113-115°C, 45 secondes

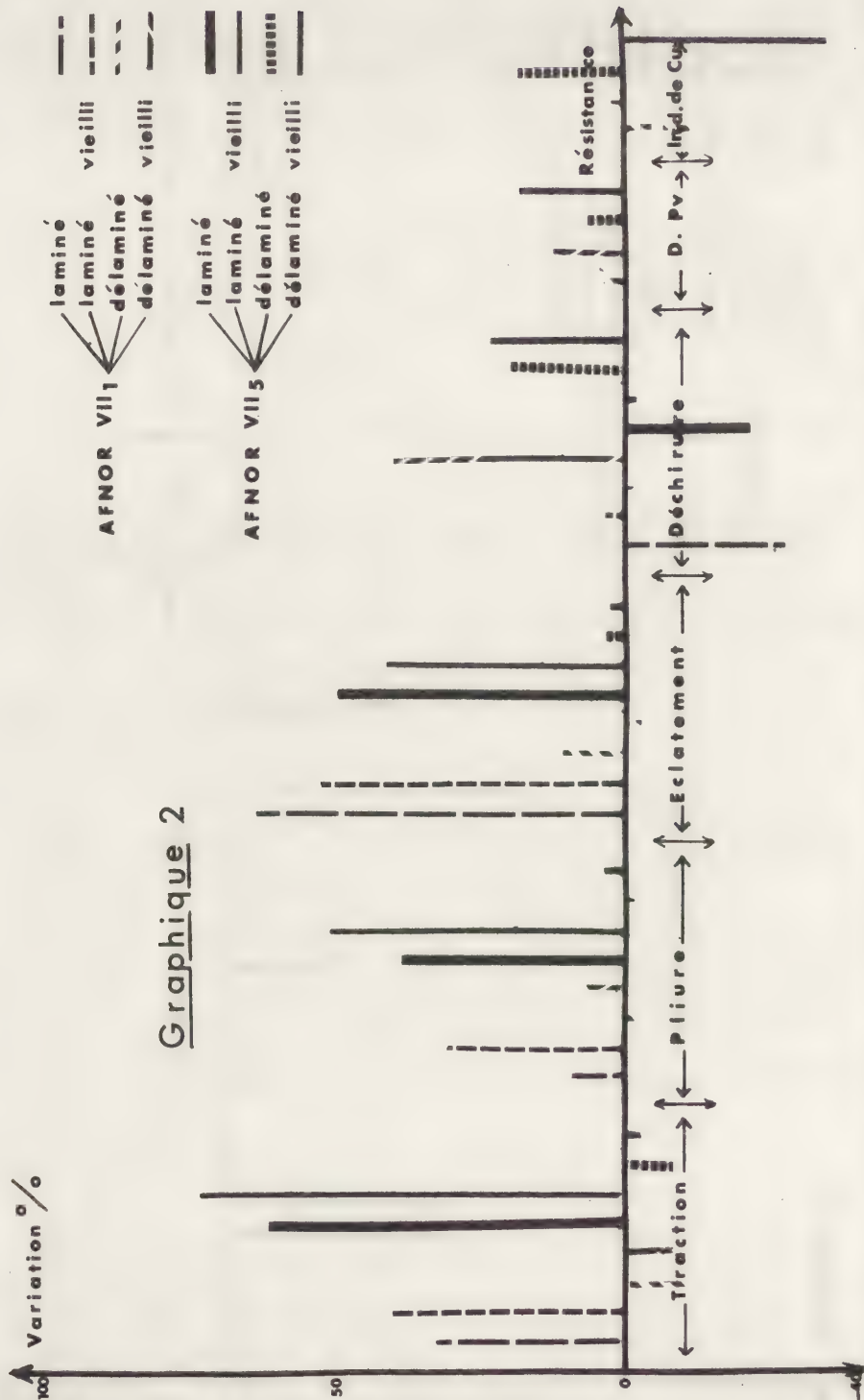
Méthodes		Blan- cheur	pH	Gram- mage	Epais- seur
1.1.	Témoin	79	5,5	80	0,12
	Laminé	64	7,8	165	0,20
	Dé laminé	71	8,0		
	Témoin vieilli	75	5,2		
	Laminé vieilli	64	7,6		
	Dé laminé vieilli	70	7,4		
	=====				
	Témoin	80	6,3	160	0,26
	Laminé	73	7,7	250	0,32
	Dé laminé	76	7,7		
1.3.	Témoin	79	5,5	80	0,12
	Laminé	70	7,9	170	0,20
	Dé laminé	76	7,8		
	Témoin vieilli	75	5,2		
	Laminé vieilli	70	8,0		
	Dé laminé vieilli	75	7,3		
	=====				
	Témoin	80	6,3	160	0,26
	Laminé	74	8,1	245	0,33
	Dé laminé	79	7,5		
2.1.	Témoin	79	5,5	80	0,12
	Laminé	77	7,1	145	0,19
	Dé laminé	80	6,1		
	Témoin vieilli	75	5,2		
	Laminé vieilli	74	7,2		
	Dé laminé vieilli	79	6,5		
	=====				
	Témoin	80	6,3	160	0,26
	Laminé	79	7,4	230	0,33
	Dé laminé	80	6,2		
Afnor VII ₅	Témoin vieilli	79	6,1		
	Laminé vieilli	74	8,0		
	Dé laminé vieilli	78	8,0		

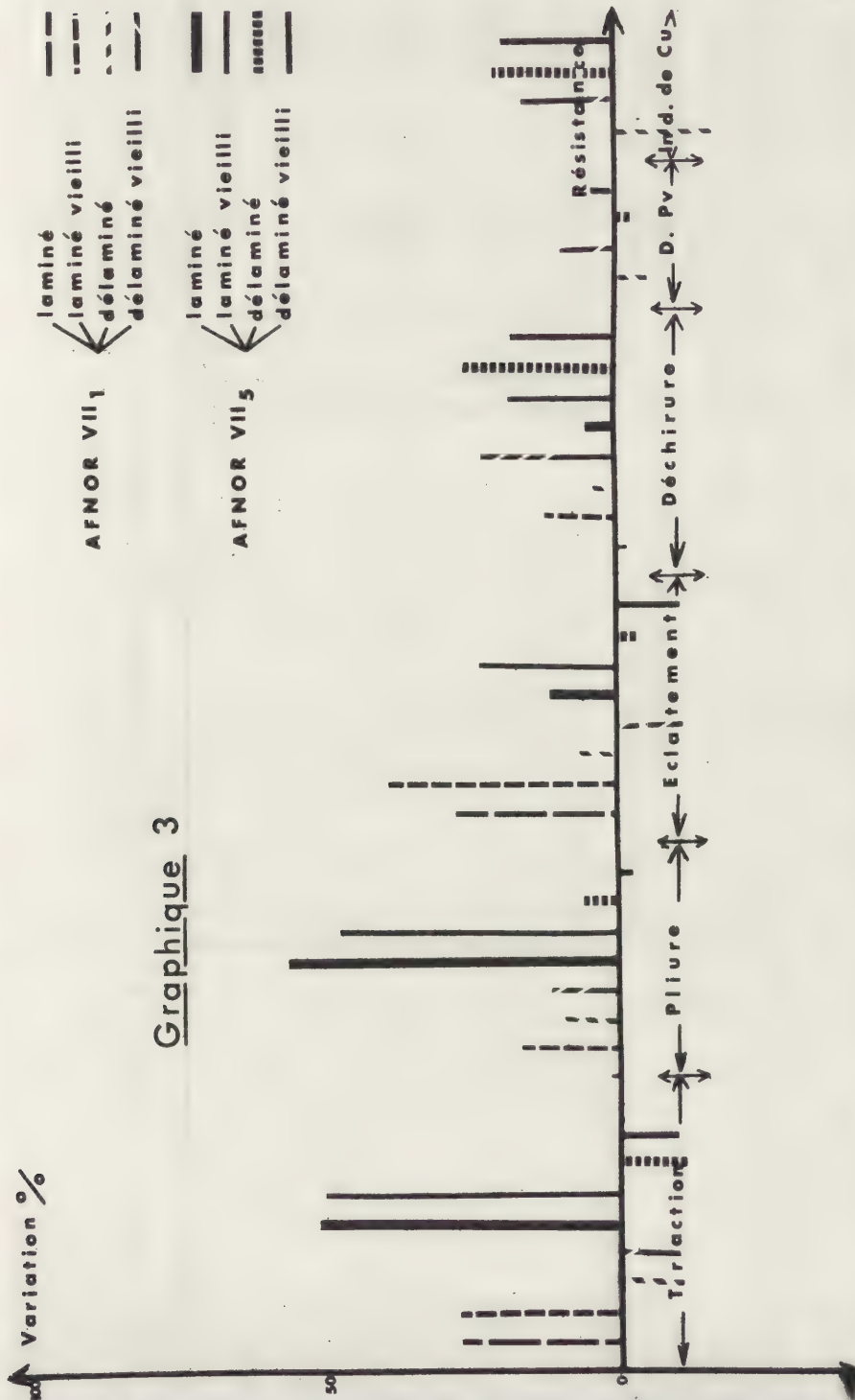
Méthodes		Blan- cheur	pH	Gram- mage	Epais- seur	
3.2.	Témoin	79	5,5	80	0,12	
	Laminé	77	8,3	165	0,22	
	Dé laminé	77	8,0			
	Afnor VII ₁	Témoin vieilli	75	5,2		
		Laminé vieilli	73	8,4		
		Dé laminé vieilli	74	7,9		
	=====					
	Afnor VII ₅	Témoin	80	6,3	160	0,26
		Laminé	78	8,0	245	0,35
		Dé laminé	78	7,9		
		Témoin vieilli	79	6,1		
		Laminé vieilli	75	7,9		
		Dé laminé vieilli	80	7,6		
=====						
4.1.	Témoin	79	5,5	80	0,12	
	Laminé	70	5,5	140	0,20	
	Afnor VII ₁	Témoin vieilli	75	5,2		
		Laminé vieilli	71	5,0		
	=====					
	Afnor VII ₅	Témoin	80	6,3	160	0,26
		Laminé	76	6,3	220	0,33
		Témoin vieilli	79	6,1		
		Laminé vieilli	76	5,8		
	=====					
	4.5.	Témoin	79	5,5	80	0,12
		Laminé	78	5,1	140	0,20
		Afnor VII ₁	Dé laminé	76	5,6	
Témoin vieilli			75	5,2		
Laminé vieilli		75	5,0			
Dé laminé vieilli		77	5,5			
=====						
Afnor VII ₅		Témoin	80	6,3	160	0,26
		Laminé	80	5,3	220	0,31
		Témoin vieilli	79	6,1		
		Laminé vieilli	79	6,4		

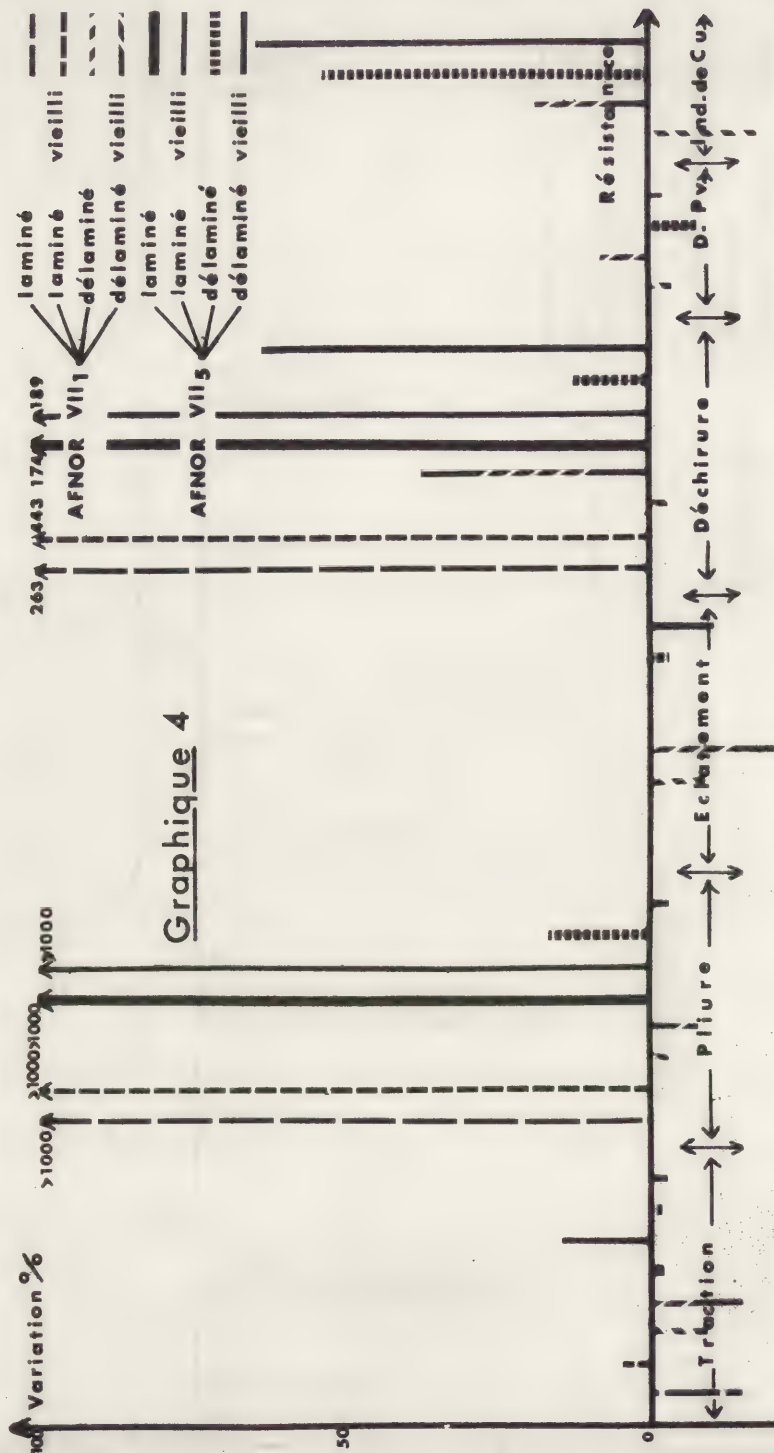


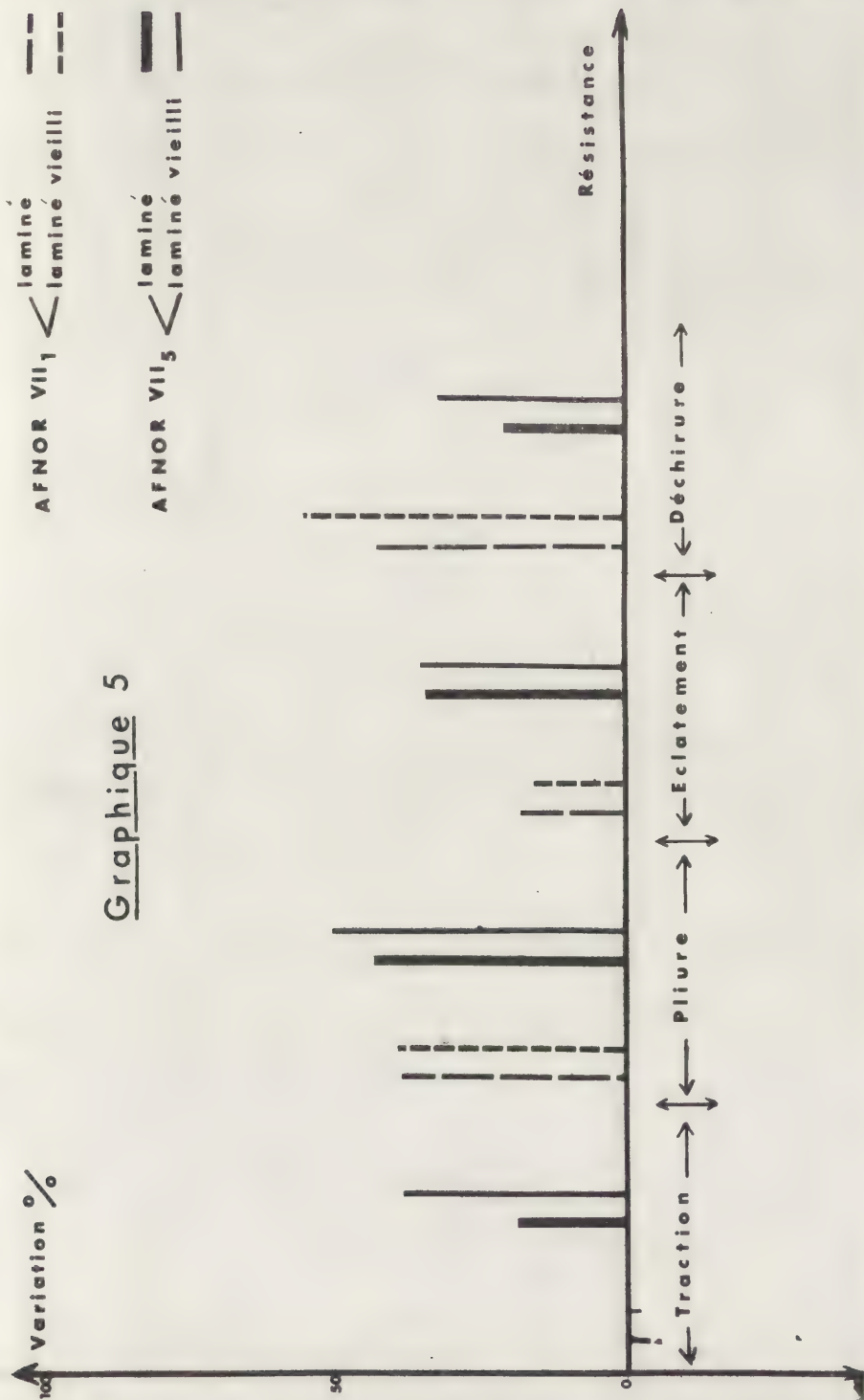
Graphique 1

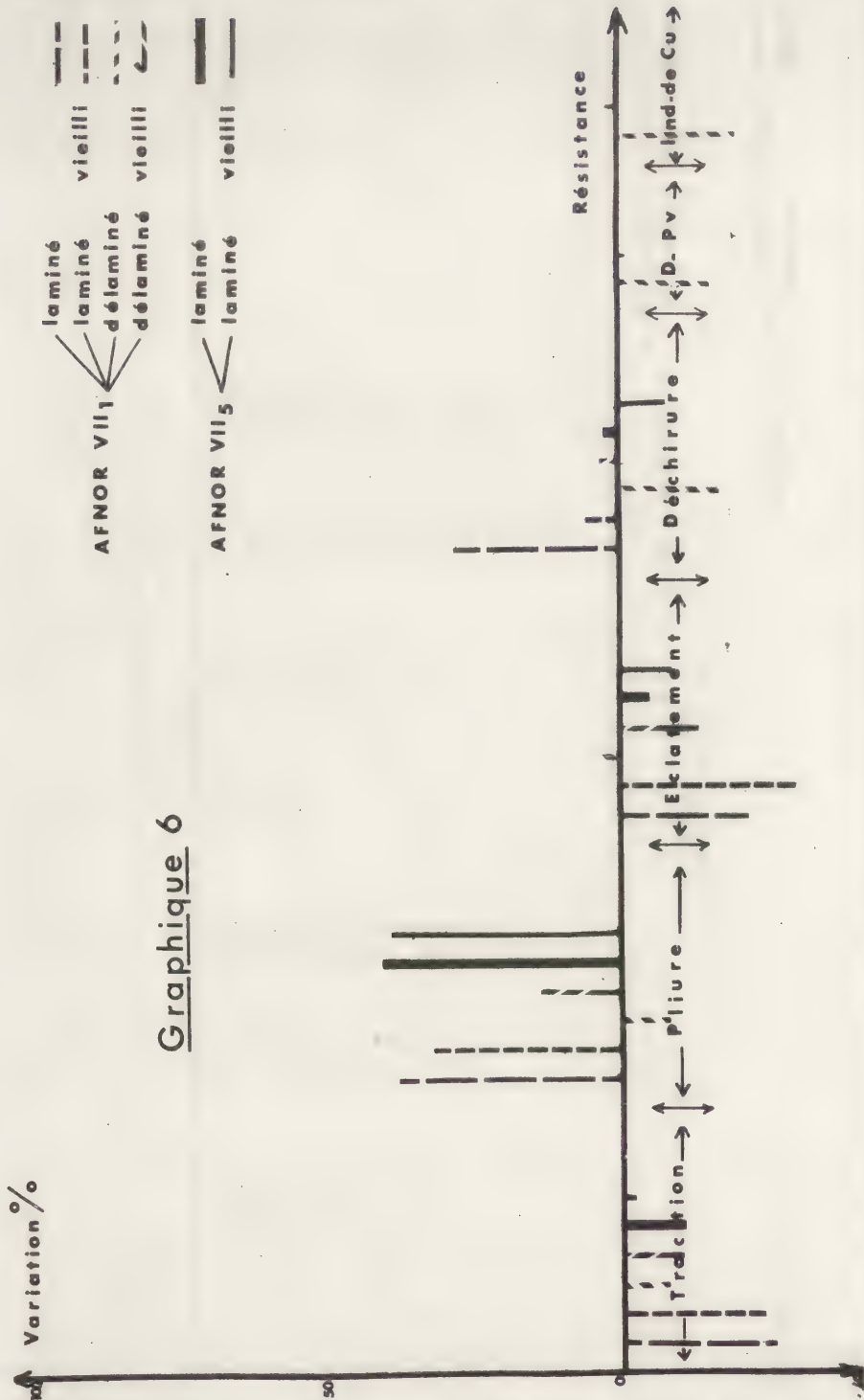












Graphique 6

LIMP VELLUM BINDING AND ITS POTENTIAL AS A CONSERVATION TYPE STRUCTURE FOR THE REBINDING OF EARLY PRINTED BOOKS A Break with 19th and 20th Century Rebinding Attitudes and Practices

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ABSTRACT: One of the positive results which developed from the disastrous flood of Florence in 1966 was the author's awareness that so-called limp vellum binding structures, although often badly damaged in their covers, had seemingly not inflicted as much damage to their text blocks as had other binding structures. Over the past eight years the author has been experimenting with this type of structure in order to assess its potential as a conservation technique. Two findings are important. First, limp vellum bindings have the potential of satisfying many conservation principles, the most interesting of which is that as non-adhesive structures they provide an opportunity for disassembly, maintenance, and reassembly with little or no damage to the text block. Second, some of the techniques may be transferrable to stiff board work, opening new avenues for development of binding techniques. This paper discusses selected aspects of the author's work with limp vellum binding structures. It is drawn from a two volume study entitled "Limp Vellum Binding."

INTRODUCTION AND HISTORICAL BACKGROUND

While handling and sorting many thousands of books which had been damaged in the November 1966 flood in Florence, I noticed that a surprising number of small limp vellum bindings of the early sixteenth century appeared, after 400 years plus at least one damaging flood, to have survived in a good state of preservation compared to other more elaborate binding structures. This observation prompted me to analyze these limp vellum structures and to study them for their feasibility for modern conservation binding.^{1/} As a result of this research it became apparent that the simplicity of construction, light weight, mechanical yielding qualities, and lack of distortion in varying atmospheres, plus the durability of its component materials, showed clearly a potentially sound conservation binding. In addition, these limp vellum structures achieve a balance between sound sewing construction and a flexible, durable, limp cover, the whole technique using little or no adhesive and having the character of a tied bundle. They also have

the great advantage of supplying one with the opportunity of designing a reversible covering technique; a cover which later generations may easily and without damage to the text block remove and replace with fresh material without the need for resewing.

Before discussing in detail several of the advantages of limp vellum structures in conservation binding, it is necessary to clarify briefly their construction. As shown in the expanded diagram in Figure 1, gatherings were sewn onto alum-tawed thongs (a) and a parchment liner (b) was placed across the spine. The head and tail bands (c) were sewn through the book and the spine liner. Then all thongs were laced back through the vellum cover (d) and the parchment liner entwining the whole together so that the text block was locked firmly, creating a 'bound' rather than a 'case' binding. The appendix gives basic terminology for limp vellum bindings.

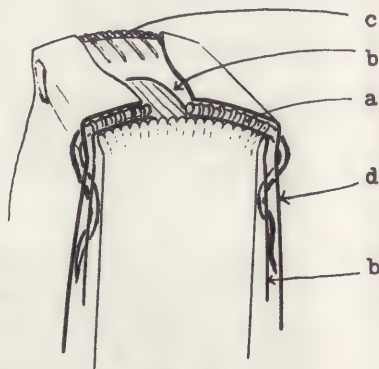


Figure 1.

The phrase 'history of bookbinding' appears nowadays to be synonymous with the study of the finishing decoration only. The subject is in fact far larger and more exciting, for the study of binding construction reflects the history of man's ingenuity when applied to a mobile, complex subject such as the codex form. Limp vellum and non-adhesive bindings were a major feature in Medieval Europe. While bibliographers have categorized the very early limp vellum bindings as cheaper versions of the more deluxe stiff board and thonged bindings of this period, I believe this to be entirely wrong. While some of their characteristics have been influenced by contemporary stiff board thong binding, the basic structure strongly reflects two essential independent influences, one being Near Eastern bookbinding techniques and the other being the vellum wrapper, said to have been used from early times as a form of protection for books which were sewn but with unattached boards. Many manuscript books are described in contemporary records as unbound (uncovered?) and others were bound long after they had been written.

By the thirteenth and fourteenth centuries, as a result of such developments as the growth of universities, the demand for books placed heavy pressures on supply. Alongside the unbroken tradition of monastic binders working with both stiff board as well as non-adhesive vellum structures, grew the secular tradition of professional binders working with several structural techniques. In addition, amateur craftsmen, such as the scholars who did their own copying and binding, brought forth important innovations and influences. In this way production of many varieties of binding techniques evolved, from simple utilitarian methods to the rather

exotic and complex techniques which appear to have mixed and moved freely between different cultures and understandings of codex construction. The subject is incredibly diverse and a multitude of undercurrents and influences can be found.

Limp vellum bindings came into their own at the time of the first printed pocket editions, for which they were so admirably suited. Occasionally fine examples are found still extant, particularly in Italy. At their finest, their success can be explained by utility and a complete mastery over tools and materials. In the first decade of the 16th century, Venetian printers began to produce pocket sized editions. Many were bound in a workmanlike, unpretentious style in which the binder achieved a harmony of composition, structure, and technique by using strong sewing construction and a flexible, durable limp vellum cover with little or no adhesive. There is little evidence to show that modern trade practices in 'extra' binding have their roots in these medieval craft methods; they are apparently an outgrowth of the 17th and 18th centuries grafted onto the medieval craft, using only its technical terms and symbols.

Quite soon after this high point had been reached, a transitional period developed when workmen displaced craftsmen. This change was due in part to the increasing pressures of work and also to the demand for large quantities of identical copies which allowed production to be split into specialized sectors; techniques were gradually standardized through repetition and economy of effort. As stocks of suitable, supple covering materials were exhausted, all kinds and qualities of parchment and vellum were utilized, including pages from manuscripts. By the middle of the 16th century we find what might be described as a case binding with lacings more for decoration than for structure, with pasteboards being used more and more, converting them into semi-limp bindings. Particularly noticeable is the thinness of the vellum skins used and the fact that only the end papers, endband cores, and its small size and light weight are keeping the volume intact.

Towards the end of the century, a rather extraordinary transformation took place, for these books suddenly appeared in refined and very luxurious circles. The covers were often cased off the book and decorated with gold-tooled and hand painted designs--the coming of age, as it were, into the High Renaissance spirit of this binding style. This developed, however, alongside the general failure to retain or to recognize the fundamental harmony between composition, technique, and purpose. Perfection of form bred, as it usually does, artificial and adventitious elements which were unrelated to the needs of these binding constructions.

For those concerned with the safekeeping of early limp vellum structures, a valuable lesson can be found here. Since examples of this later cased work have surface decoration, they are more likely to be retained than are the structurally more interesting earlier bindings.

TECHNICAL INNOVATIONS IN BRIEF

As a result of both my historical observation upon binding structures as well as my own experiences utilizing such ideas in conservation, I have developed a tentative set of criteria for establishing standards in rare book conservation. Unlike paintings or prints books are three dimensional, mobile objects. A term such as 'book conservation' to me does not simply imply the repair of the text block and rebinding for normal use in a 20th century library, but it also implies the restoration of qualities of movement such as ease of opening, spine flexibility and leaf flow. The preservation of the actual tactile qualities of vellum, leather, board, paper, type impressions, etc., are vital. In addition reliability over a long period depends to a large extent on simplicity of construction, ease of movement, and materials which are chemically, physically, and visually in harmony with one another and with the text block.

In evolving the techniques for the structure, I am experiencing many of the problems which seemed to have bothered the earlier craftsmen; and several innovations have been tried to find a more satisfactory way around them. The aim is not to make facsimile copies, but to create a new and improved structure which gives adequate scope to the conscientious book restorer. The construction and techniques used should be readily understood by future preservation personnel and recoverers, so that they will not inadvertently cause undue damage to the text block.

The chief points in the limp vellum technique so far developed are as follows:

1. Careful choice of alum-tawed skin for thonging, related to the expected flexibility of the bound leaves. Most commercial skins have proved quite inadequate for such an important function.
2. Firm sewing around double or single thongs, often with various types of 'linked' or 'packed' sewing and sometimes sewn with supported tail and head 'end-of-spine' bands (Fig. 10), a development I experimented with, starting in 1967.
3. End-band tie-downs firmly hold the head and tail of a wide, full-length spine liner.
4. Careful consideration is needed in the choice of the weight of a vellum skin in proportion to the volume's flexibility.
5. The covering process is a completely dry one, consisting of scoring, folding, cutting and interlocking.
6. Given the uncertainty of the tear-resistance of modern skins, every slot made is terminated with a punched hole. This feature can with care supply its own particular character to a binding (Fig. 2)
7. Thongs are laced through the cover and back through the cover and the liner to create a 'bound' rather than a 'cased' book (Fig. 1).

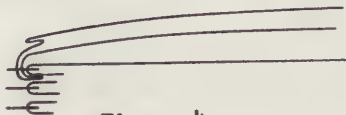
Figure 2.



Figure 3.



Figure 4.



8. Punched holes, through which the alum-tawed thongs pass, are made smaller than the thickness of the thong. When a thong is passed through and flattened, it is firmly held by the hole (Fig. 11). No other material so far tried out achieves this sort of locking effect, which may then be dismantled and reassembled in the future if necessary.

9. A soft 'yapp' edge gives rigidity to the fore-edge of the book and also leads the way into a book stack and remarkably protects the binding if dropped on the fore-edge.

10. Fore-edge ties help to hold the book as a bundle, but some librarians object to their awkwardness, and several alternatives are being tried.

When one is designing a style of binding for use in conservation, one must build into it techniques which are highly variable and flexible within themselves, for each book is an individual problem.

I shall now concentrate on a few selected innovations in my techniques, based upon observations of medieval limp vellum binding. The first deals with end-leaf design.

A good growth and flow to a book starts and finishes with the end leaves. Their connection with the cover must be in sympathy with this general action. The large lectern type book should open wide ('throw out') and stay at any page right to the very end; and it should close firmly and squarely with that delightful air-expelling 'bloomph.' But the limp vellum binding is often at its most satisfactory when used for smaller volumes: It is not for the lectern, but is most comfortable in the hands with the structure opening easily and the covers yielding and adapting to the touch. I feel that the flow through a limp vellum book starts with the covers and not with the fly-leaves; when closing, the book expells air slowly through and around the covers. For the text block to be adequately protected, limp covers must always be under a certain inward tension across their width. In our modern tradition such a direction to the covers is obtained by a 'paste-down' type end-paper, which shrinks upon drying and so adds the required tension and a certain added vertical rigidity to the cover. In such ways end leaves are important to the success of a limp structure. A common end leaf design used in limp vellum bindings during the Medieval period consisted of a folio or two separate sheets hooked

under the first and last gatherings and sewn in with the rest of the text block (Fig. 3); in stiff board work a parchment reinforcement was often added. The end leaf or paste-down of end paper usually was attached to the inner side of the cover.



Figure 5.



Figure 6.

In 1967 when I first began my experiments in developing limp vellum binding structures for the Biblioteca Nazionale Centrale di Firenze, I used this hook under gathering type of end paper construction. The directness and simplicity and close connection of the end leaf with the text block was what attracted me. In limp vellum bindings of the type described, the main hinging point is on the spine fold, the joint fold adding only a certain direction to the cover. Therefore when one of these hooked end leaves was pasted down, tensions occurred upon opening. I got over this by designing an end paper with an expanding gusset on the end leaf (Fig. 4). But I was never happy with this design for several reasons. I no longer had a closeness of cover and text block at the hinging point. Because paper and vellum behave differently in varying atmospheres, I was obtaining a certain distortion in my tests (though nothing like the amount one obtains in stiff board vellum structures), and more important, in pasting down I was sacrificing future advantages in preservation maintenance.

In my studies I noticed that several limp vellum bindings of the early 16th century appeared never to have had their end papers pasted down; in fact with some I doubted whether adhering them had ever been the intention. (I have now discovered clear evidence that this was so.) Such observations prompted me to experiment with designing an end paper of a non-paste-down type, the feasibility of which I thought would be less difficult in a limp structure than in a stiff board one. Of course it has been done before in the 20th century, particularly on thin, light weight private press books, but with varying success and with text blocks of one or two gatherings only; success of course is according to the standards one sets. Here I wished to retain the shape, rigidities and protective qualities in a cover, in fact to do as well as that produced in my pasted end paper technique. If successful, a non-pasted end-leaf would have the great advantage of supplying one with the opportunity of designing a 'reversible' (in conservation terms) covering technique--meaning a cover which later generations may easily and without damage remove from the text block and recover with fresh material or simply carry out maintenance work without resewing.

The difficulties I have encountered in designing non-adhesive end leaves stem from the fact that one wishes a method to be applicable over a wide range of problems. This may be obtained by having within the method a number of techniques that can be varied

in many ways so as to suit wide differences in text blocks and natural materials. In addition to these difficulties there are several others concerned with supplying the opportunity of dismantling and reassembly.

To withstand dismantling and reassembly of the structure such an endleaf requires a stronger and more durable material than modern commercial hand made papers can supply and a material sympathetic to the concept of limp vellum binding. My experiments so far still use traditional materials. Some of the most successful are using soft alum-dressed skin from the hinge point to the joint fold and parchment from there to the fore-edge (Fig. 5). The alum-tawed material overlaps the parchment considerably both supplying a certain bulk to the cover and in conjunction with the parchment supplying a non-adhesive trap to the thong when it is passed through after covering. This endleaf goes inside the vellum cover supplying the necessary bulk and supporting qualities.

An important quality in the parchment chosen must be its tear resistance, because I obtain a non-adhesive inward tension to the cover by my fore-edge tie anchorage mechanisms (Fig. 16, 17), of which I have several varieties. In this way my best designs achieve a tension to cover between the joint fold and fore-edge and no tension across the hinging points (Fig. 6). Concertinas of Japanese papers are often used in an attempt to distribute endpaper connections into the text block. Apart from the endleaf, which becomes integral with the cover, I often use parchment fly-leaves also, the purpose of which is to add more protection to the text-block from the constructional features in the covers such as whittawed lacing and tacketting anchorages.



Figure 7.



Figure 8.



Figure 9.

There are many types of sewing structures and each one supplies to a book a particular movement, opening, or character; most have an individual role to play in the scheme of things and therefore should be recognized as such and used in solving particular book problems. In the way we now wish books to rest and handle, some sewing structures have proved more useful and durable than others; but when evaluating such structures one must recognize the conditions of a particular period and the aims or requirements a craftsman had to fulfill. For example, when considering sewing structures before about 1400 we must recognize that they were designed to be housed in chests or book presses and not to be stood vertically on a shelf. As limp vellums are not 'backed' (jointed), one aims for less swelling after sewing than is required for stiff board books. On the traditional Western

sewing frame with a flat bed and vertical bands, the swelling of a compact, evenly tensioned sewing will naturally form, with slight pressure from the fingers, a convex or a concave shape. If the tension is too great when sewing, which often happens with beginners with 'catch' sewing (i.e., where the previous section is caught up at each thong, then a concave spine is produced which only physical means can form convex and only heavy glueing and lining treatment retain, but the tensions created will never make for good support and leaf flow.

What has happened since the 1500's is that bookbinders have thought less of the basic sewing structure and placed reliance more on adhesives and outward appearances; until today a binder is often simply a shaper of glue with a hammer, having no understanding of the subtlety and nuance of sewing structures. In conservation work one needs to use minimum or no adhesive on the spine and certainly not for any structural reasons. Peter Waters and I in 1968 adapted a traditional sewing frame to explore the possibilities of sewing in the 'round;' some attempts showed certain encouraging signs toward the possibility of achieving a completely non-adhesive spine. Certainly the characteristic over-tension across the spine was greatly relieved. I have carried on with this type of experiment but still regard the technique as very embryonic and experimental, requiring a sound testing programme.

It is in my mind to suggest that if a binder of good intention should study and practice sewing on dummies with the ideal of a non-adhesive spine set firmly in his mind, after several years his technique and understanding would be so refined and improved that in many cases adhesives would revert to playing only a minor role.

The limp vellum bindings, belonging to the first decade of the 16th century, still contain fundamentals of non-adhesive structures of the previous centuries and are well worth studying. Of the Italian bindings I studied in Florence only three or four set my thoughts to developing a limp vellum conservation binding; of the rest some had different degrees of interest in this respect, while, others, usually of a later date, had none. The earliest and structurally the finest had vellum or parchment liners originally pasted to the spine. These were the full length of the spine and overlaid generously on either side. They were carefully slotted to allow the raised bands to protrude and the liner to come in full contact with the spine folds. The end band tie downs were then pierced through the liner, holding it firmly in place at the head and tail of the spine. When the adhesive eventually broke down, the liner was still held at these structurally important points. The thongs and end-band cores laced through the core and back through the cover and the liner overlays, entwining all firmly together (Fig. 1), making the liner and endband tie-downs structurally important features.

Their importance can be gauged by studying limp and semi-limp bindings after c. 1520 when the trade was stubbing the thongs to the width of the text block, only relying on endband cores to retain the cover. This was a weaker construction, but it was a quicker tech-

nique. I am often surprised how well even this type has stood up to the rigors of modern library usage and conditions.

The most common modern end band sewing is quite useless for such an important role, for it serves none of the above functions. The only real meaning it has is one of speedy decoration; for thread, usually silk, is used to both retain the core and to decorate the book at one and the same sewing (Fig. 7). In late Medieval and Renaissance Europe, decorative end bands were usually of 'compound' construction; e.g., of more than one sewing, usually two and occasionally three. The primary, which firmly attaches the 'core' and the liner to the text block, serves as part of the structure of the book; and the second sewing was sometimes a means of decoratively connecting the covering material to the text block at the extremities of the spine. At other times it is purely decorative, using colored silks or threads and often incorporating cores of twisted thread covering the primary sewing to the width of the text block. The primary sewing had back tiedowns which made for a firm attachment and also allowed any weight of core to be used without restricting the sheets from opening under it (Fig. 8). Limp vellum binding construction having no 'backing' joints, I use the end band sewings to help set or retain a convex shape to the spine.

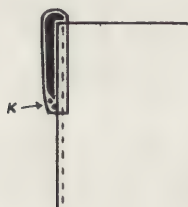


Figure 10.

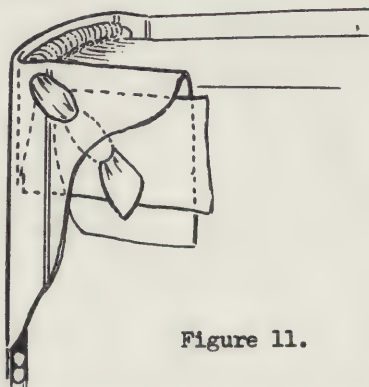


Figure 11.

The 'end of spine band' was an idea which developed out of studying several 14th and 15th century bindings, where long stitching at either end of the spine served the dual purpose of sewing gatherings together and retaining a limp cover around them. Sometimes wood, hide or a band of other material is placed between these long stitches and the cover (Fig. 9) or between the cover and spine folds of the text block directly to a limp vellum cover and without the use of semi- or inflexible materials at the spine. My main objection to it as a conservation rebinding method is the difficulty one has in obtaining a smooth flow of the leaves and after much handling it develops separate gathering movement.

The reasons which stimulated me in progressing into this new field were the fact that on some weightier text blocks I desired to unobtrusively add more support and also smaller squares to my cover. I wanted to achieve these ends without resorting to additional piercings of the text block spine folds. I achieved this by filling

in the whole area from the kettles to the ends of the spine (Fig. 10). In Medieval technique this is often a short distance. I now have several different techniques executed on and some off the sewing frame.

Conservation quality binding materials are our greatest problem. When observing the inferior quality of modern leathers and skins, it may be difficult to appreciate what an extraordinarily versatile and long-lasting material animal skins are capable of producing. No synthetic material has the profusion of potential characteristics required for such a simple structure as limp vellum bindings. If materials other than skin products are used, one finds it necessary to complicate considerably the techniques and structure. Skin is unique because, according to the processing, it can supply both abrasive resistance and suppleness, incredible strength with softness, directional rigidity with flexibility. It can be elastic yet tough, tenacious yet not harmful to a text block. Most important of all, it is capable of being extremely durable. For many years now I have felt that we have more chance of obtaining acceptable quality with vellum and alum-tawed skins because the processing is still reasonably close to the early proven techniques and far simpler than with modern leather manufacture supplying us the opportunity of setting standards and specifications. Commercially I have not obtained the quality that I require. Perhaps because today uniformity in such a natural product simply means an acceptance of a 'standard' tailored to the lowest skin quality chosen; the exact opposite of processing to retain the particular qualities of a skin.

Time is short here to discuss the different qualities one may achieve in vellum and alum-tawed processing. I will simply list here the type of qualities I require for different parts of a limp vellum structure.

Ideally, one requires three different properties in alum-dressed skin. One's needs for the thongs are for a sound supporting material, stout (not elastic), flexible in one direction and strong, with all qualities needing to be extremely durable, for ties a more pliable and soft material, and for the protection patches I use on my slotted spine designs one requires a good abrasive resistant grain surface. There is more to the character of a covering vellum than simply the color and texture; at its best vellum is a wondrous material, delightfully variable in its tactile pleasures. It has translucent depths and if left natural thickness it imparts unique and subtle handling properties. A grain split has lost many such qualities and a binder who thinks of limp vellum binding as purely economic--or worse still as a 'casing' type structure--debases it. It must be understood that the qualities inherent in the individual skins will, with understanding, become an essential part of the character of the volume's handling and movement as well as colour and texture. The ability of a vellum cover to move and flex with the text block is essential and a fundamental point of my theory of limp vellum binding. Also fundamental is that the vellum should be rigid enough to support the volume in normal use. The fact that one can reactivate the fibril bundles in specific areas, obtaining

and setting a rigid, girder-like fold or have complete flexing if one wishes, make vellum an ideal material. The type of flexibility required for a covering material depends upon qualities of substance and thickness. The actual thickness of skin which can be and should be used is difficult to convey in words. I use heavier skins than most binders would think possible to use, and in the way of working, model it onto a text block. It is difficult to convey weight of a 'full thickness' skin. Even the term is misleading, for this quality of vellum, unlike leather, can vary enormously and has little to do with age or size of animal, but with processes of manufacture. 2/

Since 1967 much of my work has been taken up developing non-adhesive covering techniques. They are gradually becoming simpler and thereby gaining more character. The basic techniques are ones of cutting, slotting and tacketting. I do not propose to go into a lengthy discussion of these techniques, as I have now covered the subject up to 1970 in a lengthy training film.^{3/} I will therefore briefly note the main features of some techniques. After selection of vellum skin to suit the particular text block, I edge around it, select the correct width of folder and form generous head and tail turn-ins. The appreciation of fine folding is important to achieving a successful result. My fundamental idea from the early days was that a limp vellum structure could have covers of a quality other than folded paper, in fact towards a board-like movement. I aim to create a section through the cover which has a slight domed appearance to its exterior. I then mark out the spine and joint and cut the slots for the thongs and the endband cores.

Often the 15th and 16th century binder damped the previously rolled thongs and laced them through slots or bodkin holes in the cover and liner, then unrolled and flattened the end of the thong inside the cover. When dry, the end of such a thong would never pull back through its hole. I cannot justify this method as it makes disassembly more difficult, so I carefully select the right size hole for the particular whittawed thong. If the vellum is of good quality it will not tear, but grip the thong firmly, and the second hole, further in, I make smaller so that a sound anchorage is produced. The design of a non-adhesive connection between the 'end of spine' bands and the cover sets an interesting problem for which I eventually (1968) found a simple solution (Fig. 11).

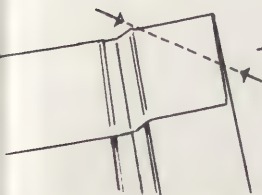


Figure 12.

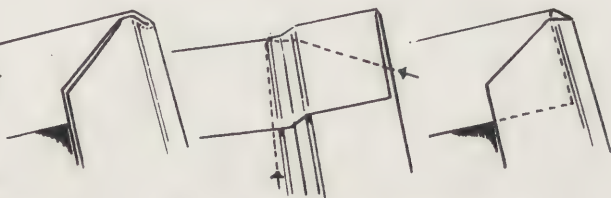


Figure 13.

The late medieval binder used several different corners (typical ones are shown in Fig. 12 and 13), which are simple, but the soft yapp tends to open up as the paste-down pulls at the fore-edge turn-in. This was an immediately recognized problem, so we had to design a corner which held the yapp closed while the fore-edge turn-in was drawn upon. Two designs proved reasonably satisfactory. I called them the 'mitred yapp' corner (Fig. 14), which has a square silhouette, and the 'tab yapp' corner (Fig. 15), which can be shaped away from the square appearance. Both of these corners are fussy and they disturb the rhythm of a technique and therefore look out of place. So, occasionally during the past seven years I have been designing simpler versions which might look and work better.

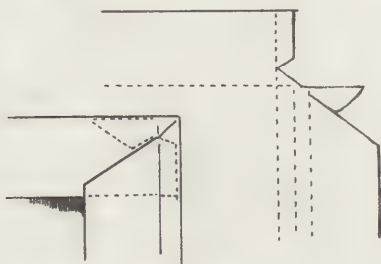


Figure 14.

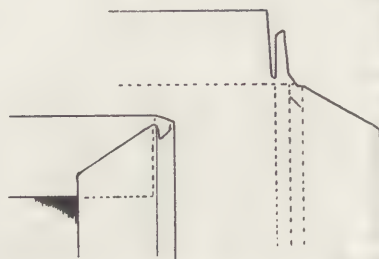


Figure 15.

By the 16th century, fore-edge tie anchorage designs were numerous and varied, and I have attempted to group them. I show some examples here (Fig. 16). A two-hole method with anchorage on the exterior of the cover I suggested for use because it is less bulky against the text block and could also be easily replaced if broken (Fig. 17).

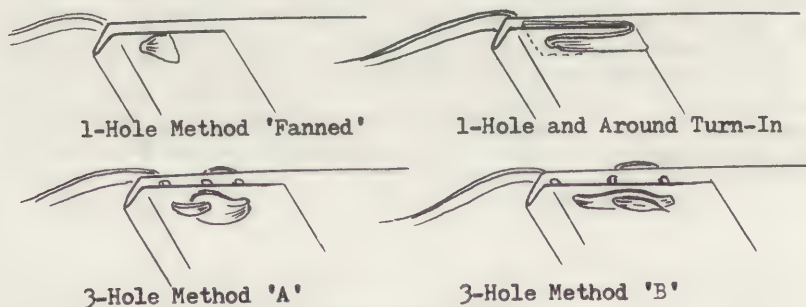


Figure 16.

For non-adhesive ends the fore-edge tie anchorages serve also the purpose of tackets in retaining the inner tension to the covers. Of the methods of fore-edge fastening I use two, the laces which tie in a bow and the peg and frog (Fig. 18). Both have a slight disadvantage; with the bow tie many people do not find the patience to tie it and with the peg and frog fastening is the Oriental tradition and not the occidental, which from the point of view of con-

servation may be regarded as an advantage or a disadvantage. But the peg and frog has certain points to recommend its use. If well designed and executed it can be very readily understood by a lay reader, and it supplies just the correct pressure to a text block.



Figure 17.

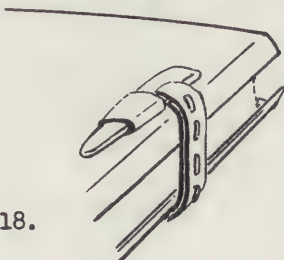


Figure 18.

SUMMARY AND CONCLUSIONS

Of all the ways of binding, possibly the limp vellum is the type which will, to the more sensitive binder, show up faults in construction most readily. But it must be understood that it has quite a different flow and handle than the stiff board book. At its most satisfactory it is a binding for the hand and lap, not the table top. But then many bindings should be thought of in this way, particularly the smaller proportioned ones. For example, the many late Medieval Books of Hours or the 16th century pocket editions, which are to a certain extent destroyed when forced to fit modern library requirements.

This report has stemmed from a desire to recover many Italian limp and semi limp vellum bindings which had been damaged and had lost their covers in the Florence flood of 1966. I never will condone the destruction of original binding structures or coverings however badly damaged they may be, for generally I am convinced, more than ever, that the future use of such original limp vellum bindings is intrinsically within the historical object itself.

To return to the theme of this talk, I do not wish to imply that I always use quite original techniques and materials on early books, in fact I am very wary indeed of so-called improvements which change the visual or tactile character of a volume. There are certainly many suggestions which fall into such a category put forward by people who have little understanding of craft ability or the value of such objects to future generations. Also I am opposed to cosmetic treatments of any kind, such as is increasingly being carried out. I am rather in favor of leaving well alone and boxing comfortably until such time as finer materials and improved research and scholarship can be brought to bear upon the individual problems.

I have been asked several times how I justify using a few quite original techniques of construction on early printed books, a question which appears to suggest that the techniques commonly used in the better workshops today are contemporary with the particular period of the book. This of course is not so. The late Medieval binder came at the end of a very long period of experiment, changing techniques and awareness of a creativity and variety of codex construction, the likes of which we have never seen since. To me, his

thoughts and endeavors appear totally different to those of present-day bookbinders. Instead of looking backwards, my endeavor is to attempt to understand the developments and influences upon him. This is difficult, for an extremely wide knowledge is of course necessary; but I believe it is an attitude which will attract and bring creative young talent into the field. The delight to be found in a study of pre-1550 binding structure is very much of the 20th century, for there is this genuine fascination with how tools, materials, and structures influence the character and design of objects.

Notes:

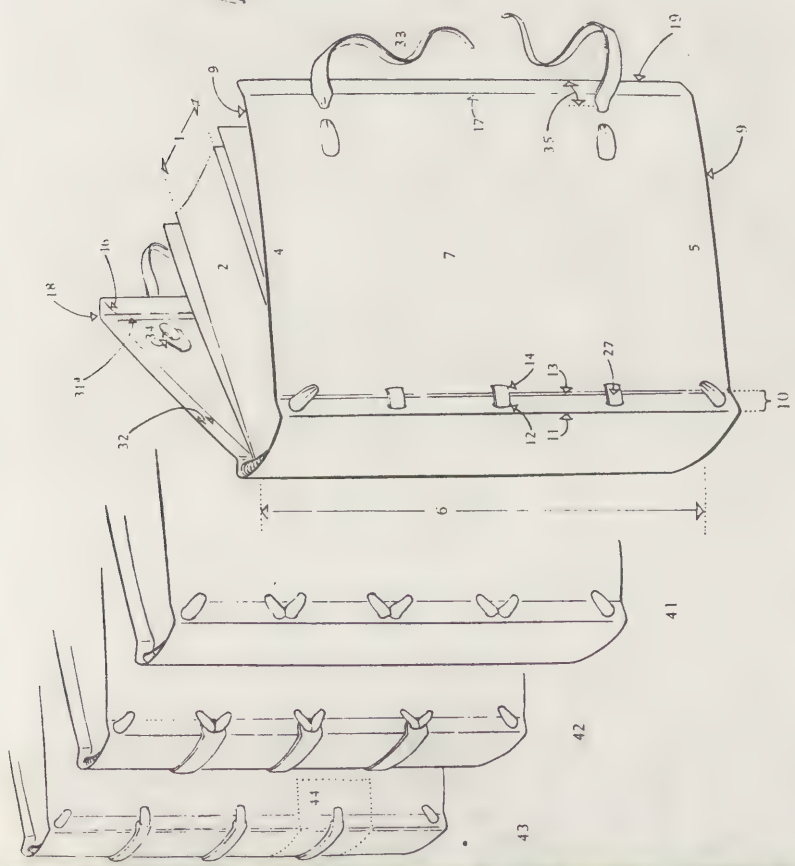
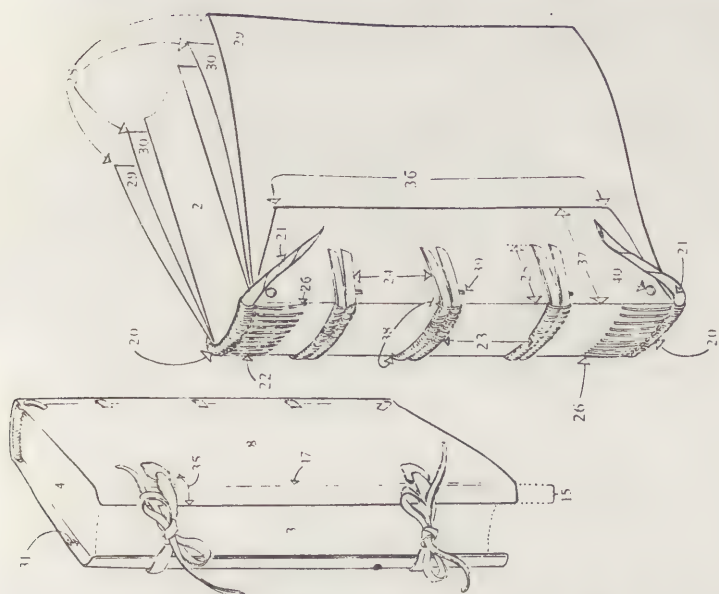
1/ I was encouraged to continue the studies and experiments by Tony Cains, Peter Waters, and later by Roger Powell and Sir Frank Francis. It became obvious that such a study was becoming increasingly broad in its scope and important in its relevance to conservation binding. The Council on Library Resources, Inc., Washington, D. C., generously supplied a grant which in part has allowed my research and experiments to continue up to the present stage. Out of this study grew two volumes of text supported by over 1000 photographs and 6 short films illustrating not only historical book structures but also technique and conservation procedures, samples of vellum skins made to different specifications to illustrate various qualities discussed and dummies of different book structures.

2/ Note the variety of thicknesses of the vellum samples enclosed with my CLR report (see note 1) all of which are processed from two types of animal of similar age, size and weight of skin and all are 'full thickness.'

3/ 'Limp Vellum Binding,' by C. Clarkson, a film made in Roger Powell's studio in England and graciously funded by the Library of Congress, Washington, D. C.

APPENDIX: Basic Terminology for Limp & Semi-Limp Vellum Bindings
Terms are keyed to drawings on p. 15.

- | | | |
|------------------|-------------------|-----------------------------|
| 1. Text block | 16. Yapp mitre | 28. Endpaper |
| 2. Book-edge | Tab yapp | 29. End leaf |
| 3. Fore-edge | 17. Yapp score | Paste-down |
| 4. Head | " fold | 30. Fly leaf |
| 5. Tail | 18. Yap interior | 31. Square |
| 6. Spine | Score/fold | 32. Paste-down square |
| 7. Upper cover | 19. Fore-edge | 33. Tie |
| 8. Lower cover | Score/fold | 34. Tie anchorage |
| 9. Turn-in score | 20. Endband | 35. Tie overlay |
| 10. " " fold | 21. Endband | 36. Spine liner |
| 10. Joint | Core | 37. Liner overlay |
| 11. Spine score | 22. Tie-down | 38. Liner/Slot |
| " fold | 23. Sewing | 39. Liner endband |
| 12. Spine slot | 24. Spine band | Slot/Hole |
| " hole | 25. Slip | 40. Liner band |
| 13. Joint score | 26. Kettle stitch | Slot/Hole |
| " fold | or hitch | 41. Branched lacing |
| 14. Joint slot | 27. Lacing | 42. Overband |
| " hole | | 43. Slotted cover |
| 15. Yapp | | 44. Sewing protective piece |





THE EFFECT OF CHLORAMINE T ON PAPER

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ABSTRACT

In restoration workshops various bleaching methods are used. One of these methods employs a mild bleaching agent, chloramine T. Often this technique is used without rinsing after bleaching. Our research was initiated in order to find out whether the residues of this bleaching agent add to the deterioration of the paper. In order to compare the results properly some other standard bleaching methods were included in the research. Three kinds of paper were treated with the various bleaching methods, aged by heating and tested on folding endurance, whiteness, pH and degree of polymerisation.

From these tests we could conclude that residues of chloramine T are indeed dangerous for paper. Another important observation is, that rinsing with water, gives more strength to paper.

INTRODUCTION

In the restoration studios of numerous museums and archives bleaching of yellowed drawings and archive documents is a daily routine. Bleaching of paper, either partially or wholly, is generally done as part of a total restoration process, after which the objects may once again satisfy aesthetic requirements and are preserved against further degradation. Many methods (1,8,9) are used, varying in composition and concentration of the materials and in method. Nearly all bleaching methods employed are oxidative, cellulose residues being further oxidized to smaller, water-soluble molecules. Because the methods are oxidative it is probable that cellulose chains which are still intact are oxidized to oxycellulose, which means that the paper strength will deteriorate. As to the degradation of paper under different conditions a great many experiments have already been done, (4,5,6). In her book Flieder discusses at length the various possible ways of

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bleaching mouldy patches and the effect of those methods on paper (1). Wilson (5,9) also carried out various experiments on bleaching and indicated what testing methods can be used. One of the methods which is being increasingly used is bleaching with chloramine T. This is a para-toluene-sulphonchloramide sodium compound with mild bleaching properties. When oxygen is given off in 'statu nascendi' no hydrochloric acid is formed (as with sodium hypochlorite), but sodium chloride. It is due to precisely these properties that chloramine T is used to bleach very fragile paper. The procedure may be spraying, careful application with a brush or floating the blank rear of a paper object on the bleaching solution, so that the facing side, e.g. a drawing is not affected. This last method is extremely suitable for designs done in a vulnerable medium such as watercolours.

In the above-mentioned techniques the chloramine T is not rinsed off. This is a most important feature prone to questioning and comparison with other methods. Do the chloramine residues have a detrimental effect on the paper? Do the residues encourage yellowing?

Our study was limited in the first instance to answering these queries. Hence different kinds of paper were subjected to a number of bleaching processes, after which the paper was aged by means of heating. The folding endurance is determined before and after ageing. In addition the pH-value, the whiteness and the degree of polymerization are determined. Ageing due to heating is difficult to correlate with natural ageing (5); the resultant ageing phenomena are not identical, but it is still a good way of comparing the effect of the various methods. In order to be able to draw reliable conclusions, a few standard methods using other bleaching agents were also included in the study.

MATERIALS

In order to approach in testing the practical situation of restoration as closely as possible, two very different kinds of paper were originally chosen. A high-grade rag paper and a poor quality newsprint. The latter, however, gave such poor results that it was replaced by porous filter paper. Later we were able to get hold of a few 18th-century books which could be used for the study. This eliminated the common objection that experiments are usually only done with new paper.

KINDS OF PAPER

- A. a high-grade 100% rag paper "Imperium Registerpapier" from G.H. Bührmann's in Amsterdam.
- B. a 100% cellulose filter paper (laboratory quality) from P.M. Tamson in Zoetermeer.
- C. 18th-century printed paper taken from different books.

TABLE A

	A	B	C
Basis weight ASTM D 646	120 g	65 g	± 60 g
Folding endurance AFTER NEN in grain direction 1855 (D643)	1542	1243	726
Folding endurance in cross direction	1096	338	431
pH-value, surface measurement	5.4	6.5	5.0
pH-value, after ASTM D778	5.6	7.0	5.4
Whiteness, after TAPPI R457	107,5	86.0	57.5
Degree of polymerization measured as fluidity in rhés (1% solution)	1.0	3.4	12.6

DESCRIPTION OF TESTING METHODS (9)

1. Standard Method of Testing for Relative Stability of Paper (Effect of Heat on Folding Endurance), after ASTM D776-65.

First of all the folding endurance is determined after which the paper is heated for 3 x 24 hours at 105° C in a heating cabinet and then the folding endurance is determined a second time. The folding endurance is often a good indication of the degradation of the paper.

Ageing due to heat is not identical with natural ageing, although Eirk (3) states that 72 hours heating corresponds to a natural ageing of appr. 25-26 years at room temperature. Although the influence of temperature, possibly without some humidity, has been a point of discussion with many authors (4, 5, 6), the ASTM standard method can be used very effectively to determine the effects of the various methods in comparing one to the other.

2. Cuprammonium Disperse Viscosity of Pulp, after Tappi T206.

The viscosity of cellulose solutions is a function of the degree of polymerization. The degree of polymerization represents the average chain length of the cellulose. The more the cellulose is attacked, the lower the average degree of polymerization will be and this will therefore be a measure for attack by different chemicals and other effects on the paper. The degree of polymerization expressed in rhés increases with shortening of the chain length, i.e. increased attack leads to more fracture points.

75/15/4-4

Table B shows several examples of differences in the degree of polymerization.

TABLE B

Material	DP	Fluidity in Rhés(0,5%)
Cotton	3000-4000	1-2
Linen	2500	3-4
Raw Linters	1500	ca.10-15
Wood Cellulose	1000-1200	ca.20
Bleached wood cellulose	800-900	ca.30

3.1. pH-Value.

Test for Hydrogen Ion Concentration of Buffered Paper Extracts.
ASTM D778

3.2. Measurement of pH-value on the Paper Surface.

This method of measuring the pH is not destructive and is often used in museums and archives to determine whether the paper must be deacidified. Since there is no standard method a fixed method was adopted for the purpose of this study, so that the values could be compared. Demineralized water was used which had been boiled and then cooled to appr. 20° C. One drop of this water, which must have a pH of between 6.5 and 7.0, is pipetted onto the paper to be measured. An electrode with a flat bottom is placed on this moistened spot. The electrode used here was an Ingold combination electrode, type-number LOT 403-80.

The pH was recorded after 30 seconds and then again after a lapse of another 30 seconds. The treated paper was measured in this way in 3 different places, the average of the 3 readings was then taken rounded to 0.1 exactly.

The pH of paper determines its rate of ageing. Its degradation is often the result of free hydrogen-ions e.g., caused by the absorption of SO₂ from the air, alum residues, bleach residues, etc. Unfortunately the two methods, the hot extraction method and the surface method, are difficult to correlate (9). The method used most frequently in restoration studios is the non-destructive surface method.

4. Whiteness.

In a study of bleaching methods the whiteness of the bleached

paper is of course an important aspect. Since new paper is used in this study, however, the whiteness is in this case no measure for the result achieved. What is important is the whiteness after ageing, since yellowing is caused here by the presence of degradation products in the paper and is as such a measure of the degradation and the long-term effect of bleaching. The actual effect of the bleaching methods can be seen on several identical lithographs (Figs. 1,2) on which all the methods used were tested.

Bleaching Methods (1,7,8)

The various bleaching methods used in this study are all oxidative, i.e. the paper is bleached by oxygen in 'statu nascendi'. The following bleaching agents were used:

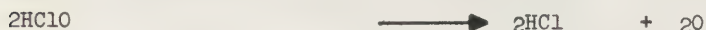
a) Potassium permanganate



The manganese dioxide (MnO_2) formed is removed by potassium metabisulphite

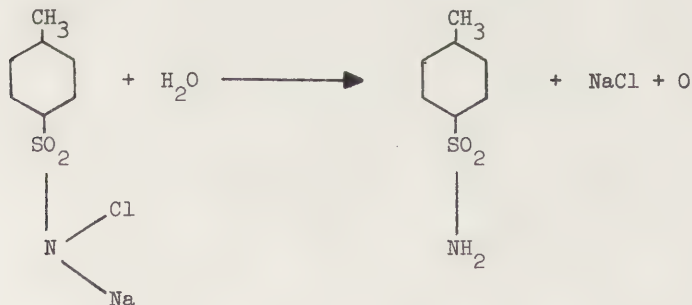


b) Sodium hypochlorite



The hydrochloric acid (HCl) formed is removed by sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) or sodiumbisulphite (NaHSO_3)

c) Chloramine T



Application of the Various Methods.

0. Untreated paper.
1. Rinse the paper for 4 hours in running tap-water and then dry between filter paper.
2. Immerse the paper for 30 minutes in a 0.1% solution of KMnO_4 in water. After this rinse for a short while with tap-water to remove the excess KMnO_4 . Then immerse the paper in a 1% solution of potassium metabisulphite in water, to remove the manganese oxide formed. Finally rinse the paper for 3 hours in running tap-water.
3. Immerse the paper for 1 hour in a solution of NaClO containing 10 g active chlorine per liter. A normal, commercially available solution is used. Briefly rinse the paper with tap-water, then immerse it for 15 minutes in a 4% solution of $\text{Na}_2\text{S}_2\text{O}_3$. Finally rinse the paper for 3 hours in running tap-water.
4. Immerse the paper for 30 minutes in a 2% solution of chloramine T and do not rinse afterwards. Leave the paper to dry for appr. 16 hours, then rinse for 1 hour in running tap-water.
5. Ibid. 4. Finally rinse in a bath of demineralised water. (This method was carried out in the Restoration Studio of the Rijks Prentenkabinet, Amsterdam.)
6. Cover the back of the paper with Japanese paper and apply over this a 2% solution of chloramine T with a soft brush. Leave the paper until it is completely dry. Repeat 3 times. Do not rinse.
7. Ibid. 6, but repeat 10 times.
8. Spray the paper on both sides with 1 ml. 2% solution of chloramine T and leave to dry. Repeat 5 times. After spraying and drying for the fifth time rinse for 1 hour in running tap-water.
9. Ibid. 8. Do not rinse.
10. Leave the paper to float for 1 hour on the surface of the bleaching solution containing 2% chloramine T. The front side of the paper must not come into contact with the bleaching solution. To ensure that the paper does not curl, the front side is sprayed with 1 ml. demineralised water. After bleaching rinse, leaving the paper to float on the surface of the water, so that the facing side does not come into contact with the rinsing water.
11. Ibid. 10, but do not rinse.
12. Immerse the paper for 1 hour in a solution of NaClO (commercially available solution) containing 1 g active chlorine per liter. Then rinse briefly with tap-water. Immerse for 15 minutes in a 4% solution of $\text{Na}_2\text{S}_2\text{O}_3$. Finally rinse the paper for 3 hours in running tap-water.

RESULTS

The results of the various test methods are marked in Tables I to VII. These tables give an impression of the decrease in strength of the paper caused by the various bleaching methods. Results acquired on testing old paper are not included in the calculations. The variation in the results makes it very difficult to correlate these with the results derived in tests on the two other kinds of paper. Tests on folding endurance, degree of polymerisation and whiteness were carried out at the Fibre Institute TNO, Delft, Holland.

CONCLUSION

Not much difference can be seen in results of the test methods 2, 4 + 5 and 12; these are respectively: the bleaching with potassium permanganate, chloramine T and a very diluted solution of sodium hypochlorite. (Table III, IV.) There is no direct deterioration after the bleaching treatment and after accelerated ageing there is no significant difference between the results of the three methods. However, it seems that the bleaching with potassium permanganate has less influence on the deterioration of rag-paper (A). On porous paper (B) the three methods do not show any difference. The bleaching effect of potassium permanganate on old paper is a little less than that caused by the two other methods (Photo 1 and 2).

The use of chloramine T without rinsing has a harmful effect on the strength of paper. In comparing the results of respectively method 8 and 9, and 10 and 11, it becomes clear that the remaining residues of chloramine T affect the deterioration of paper seriously. In comparing results of methods 6 and 7 it becomes clear that the rate of the deterioration depends on the quantity of the residue of chloramine T in the paper. The more chloramine in the paper the more degradation of the paper.

The use of water has a positive influence on the strength of paper. Comparing the results it can be concluded that the strength of the paper increases with about 25%. This increase of strength has been caused by the orientation of the fibres. Residues of deteriorated cellulose will dissolve in water and cause a higher average degree of polymerisation after the paper has been rinsed.

ACKNOWLEDGEMENT

The author is very grateful to Mr. W. van Oort, Rijks Prentekabinet, Amsterdam, for his cooperation and to Miss Ch. Wolff for her assistance in preparing some test samples.

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Table I Folding endurance after various treatments before ageing

	A				B				C			
	↑	Vc	⊥	Vc	↑	Vc	⊥	Vc	↑	Vc	⊥	Vc
0	1542	25,3	1096	12,7	1243	24,5	338	38,2	726	43,4	431	110,0
1	1866	25,8	1581	12,1	1301	35,0	501	38,6	1633	29,1	1384	60,7
2	2061	15,8	1447	21,9	1346	34,2	335	79,0	1362	43,3	761	86,3
3	1250	26,5	724	32,9	936	31,7	229	20,7	-	-	-	-
4	1890	26,3	1410	19,4	823	37,2	339	39,3	-	-	-	-
5	1870	23,1	1766	22,0	682	31,2	282	30,5	1069	30,9	334	60,5
6	1725	16,9	1095	27,5	316	41,8	92	27,6	908	31,7	285	26,1
7	1194	26,8	464	39,1	156	27,8	63	52,0	112	26,6	55	40,3
8	2035	13,9	1678	19,8	1100	19,0	359	41,0	-	-	-	-
9	1777	20,7	1230	17,4	1028	41,8	245	40,3	-	-	-	-
10	1976	19,7	1434	21,0	939	35,8	385	32,9	-	-	-	-
11	1402	30,5	1143	24,0	420	32,0	158	31,1	-	-	-	-
12	2061	13,2	1489	24,7	849	56,6	247	54,9	227	58,5	177	90,8
	Load = 900 g				Load = 300 g				Load = 250 g			



= machine direction

= cross direction

Vc = Variation coefficient

Table II: Folding endurance after various treatments after ageing

	A				B				C			
	↑	Vc	⊥	Vc	↑	Vc	⊥	Vc	↑	Vc	⊥	Vc
0	1409	21,2	956	18,9	891	39,0	302	28,0	329	63,0	151	24,1
1	1422	13,9	963	25,1	1104	41,2	688	21,7	935	42,1	631	63,0
2	1430	16,6	1103	13,1	706	42,0	243	26,0	411	36,1	245	91,0
3	47	21,8	35	13,3	513	26,4	168	36,3	-	-	-	-
4	663	22,2	661	20,9	735	30,2	240	41,1	-	-	-	-
5	609	22,5	747	18,5	738	47,2	257	29,6	422	55,2	227	31,3
6	483	79,0	530	41,5	136	24,3	68	30,9	131	26,1	47	63,7
7	177	60,0	176	33,1	98	28,6	50	38,0	45	20,4	27	23,3
8	1310	25,7	1241	21,9	801	35,6	200	27,0	-	-	-	-
9	1277	25,7	789	23,0	580	32,9	215	39,4	-	-	-	-
10	837	36,0	581	26,5	952	44,6	225	44,4	-	-	-	-
11	579	30,4	621	19,6	303	35,5	83	29,0	-	-	-	-
12	1027	18,0	631	53,6	559	42,3	207	48,2	261	64,3	50	69,0
	Load = 900 g				Load = 300 g				Load = 250 g			



= machine direction

= cross direction

Vc = Variation coefficient in %

Table III Decrease and increase in folding endurance
calculated with regard to the untreated paper.

	Before ageing		After ageing	
	A	B	A	B
0	%	%	%	%
1	+ 32,6	+ 26,4	+ 0,9	+ 75,8
2	+ 32,8	+ 3,7	+ 8,5	- 20,1
3	- 26,4	- 28,4	- 96,5	- 43,4
4	+ 25,6	- 16,8	- 41,9	- 19,0
5	+ 41,2	- 30,8	- 39,3	- 16,3
6	+ 6,0	- 73,7	- 55,1	- 81,1
7	- 40,1	- 84,4	- 84,5	- 86,2
8	+ 42,5	- 3,1	+ 11,4	- 21,9
9	+ 13,7	- 22,4	- 13,5	- 31,9
10	+ 29,4	- 5,3	- 39,9	- 9,3
11	- 2,4	- 59,8	- 47,0	- 69,5
12	+ 34,8	- 30,1	- 30,5	- 34,4

The percentages give the average between machine
direction and cross direction.

Table IV Decrease and increase in folding endurance
calculated with regard to the paper rinsed
with water.

	Before ageing		After ageing	
	A	B	A	B
1	%	%	%	%
2	+ 1,0	- 14,8	+ 7,6	- 50,4
3	- 43,6	- 41,2	- 96,5	- 64,5
4	- 4,7	- 33,9	- 42,4	- 49,2
5	- 5,8	- 45,7	- 39,9	- 47,9
6	- 19,1	- 78,7	- 55,5	- 89,0
7	- 53,4	- 87,7	- 84,7	- 91,9
8	+ 7,6	- 21,8	+ 10,5	- 49,1
9	- 13,6	- 36,0	- 11,2	- 58,1
10	- 1,7	- 25,6	- 40,4	- 40,5
11	- 26,3	- 68,1	- 47,4	- 80,3
12	+ 2,3	- 42,7	- 31,1	- 59,6

The percentages give the average between machine
direction and cross direction.

Table V: Whiteness after Tappi R457, Elrepho, xenonlight with filter R457

	A	A (aged)	B	B (aged)	C	C (aged)
	%					
0	107,5	95,0	86,0	81,5	57,5	52,2
1	106,0	92,0	86,0	80,5	59,0	61,0
2	100,5	88,0	88,5	82,5	73,5	70,5
3	98,5	76,0	88,5	82,0	-	-
4	96,5	81,0	88,0	81,5	-	-
5	98,5	83,5	88,0	81,0	72,5	68,5
6	100,5	87,5	89,0	73,0	70,0	58,5
7	93,5	78,0	88,5	70,0	77,5	60,0
8	99,0	83,5	88,0	79,0	-	-
9	99,0	84,5	87,5	81,5	-	-
10	99,0	87,5	87,5	81,0	-	-
11	98,5	84,0	89,5	73,5	-	-
12	104,5	91,0	89,0	81,0	78,0	73,5

Table VI: pH-values before and after artificial ageing

	A				B				C			
	Surface pH		Extraction pH		Surface pH		Extraction pH		Surface pH		Extraction pH	
		aged		aged		aged		aged		aged		aged
0	5,4	5,6	5,6	5,0	6,8	6,5	7,0	6,9	5,2	5,3	5,4	5,6
1	5,9	6,0	6,0	6,6	7,0	6,9	7,5	7,5	7,0	6,9	7,1	7,3
2	6,0	6,4	6,1	6,5	7,0	6,8	7,6	7,3	6,4	6,8	6,5	6,9
3	5,6	5,3	5,7	5,8	6,7	6,6	6,7	6,8	-	-	-	-
4	5,6	6,0	5,6	6,0	7,0	6,4	7,0	7,0	-	-	-	-
5	5,7	5,8	5,7	5,6	6,5	6,0	6,6	6,1	6,5	6,0	6,8	6,4
6	5,1	5,0	5,0	4,9	5,8	5,6	6,1	5,3	6,0	5,4	5,9	5,4
7	5,0	4,8	4,6	4,7	5,3	4,9	5,1	4,6	5,4	5,0	5,3	4,7
8	5,8	5,6	6,0	5,7	6,6	6,3	6,8	6,4	-	-	-	-
9	5,0	5,0	4,9	4,8	6,0	6,1	6,2	6,1	-	-	-	-
10	5,3	5,6	5,5	5,1	6,4	6,4	6,6	6,5	-	-	-	-
11	5,1	5,0	4,9	4,6	5,5	5,6	5,6	5,5	-	-	-	-
12	5,6	5,5	5,7	5,9	6,4	6,5	6,8	6,5	6,6	6,0	7,0	6,9

Table VII: Fluidity in rhé's, of a 1% solution in Cuprammonium

	A	B	C
0	1,0	3,4	12,6
1	1,0	3,5	12,5
2	2,0	4,4	11,4
3	4,4	3,8	-
4	2,1	4,2	-
5	1,3	3,7	14,3
6	1,3	21,8	13,7
7	5,5	37,5	22,2
8	1,1	4,2	-
9	1,3	4,6	-
10	1,1	4,0	-
11	2,2	10,4	-
12	1,1	3,8	12,4

75/15/4-16

PHOTO 1: Comparative bleaching methods tested on old paper.



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PHOTO II: Comparative bleaching methods tested on old paper

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WALLPAPER

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SOME EXPERIMENTS WITH HIGH PERFORMANCE LIQUID
CHROMATOGRAPHY IN ANALYSING BINDING MEDIA IN
OBJECTS OF ART

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INTRODUCTION

For the analysis of organic materials various methods can be used. The most widely employed are several kinds of spectrometry, e.g. infra-red and ultra-violet spectrometry and mass-spectrometry and also different kinds of chromatography: paper, thin-layer, gas - and high performance liquid chromatography. Some kinds of electrophoresis are used as well.

Specific problems arise in analysing organic materials of objects of art, such as the binding media of paintlayers. As the objects are not to be damaged the samples have to be minute. A second problem is that the materials used by the ancient artists were in most cases complicated mixtures. Even the so-called pure materials were contaminated by other materials. On the other hand ageing of the materials may have caused a change in composition, and in that case not all results obtained can be compared with standard materials.

In studying an object of art it is necessary to obtain as much information as possible concerning that object. For analysis of the binding media the methods used in our Laboratory are infra-red spectrometry and gas- and thin-layer chromatography.

For the analysis of binding media like oil, glues, gums and varnishes various systems are being developed. However, for some of the binding media there are methods which give better results than thin-layer chromatography. For a first check infra-red spectrometry is used too, but for the further identification thin-layer chromatography has proved to give good results. The application of chromatographical methods is meant to obtain a quick and clear answer regarding the properties of the sample.

The results of various analyses enable us to determine roughly what the media consist of. However, in analysing various animal

75/15/5-2

glues it is mostly impossible to find out what kind of glue is present in the object studied. Until now it was hardly possible to determine the difference between bone-glue and skin-glue because they both contain the same amino acids, although in different concentrations. Moreover, the traditional techniques did not allow for quantitative analysis on the small amount of samples which can be safely taken from objects of art. Therefore we have searched for other methods.

In chromatography as well as in electrophoresis some recent developments were at our disposal which promised better results in analysing proteins or amino acids. One of these methods is high performance liquid chromatography (HPLC),(1). The apparatus for this method is, however, unlike that for thin-layer chromatography, rather expensive. We therefore decided to first of all test the usefulness of the method with borrowed equipment. This was made possible through kind cooperation of Varian Benelux b.v. in Amsterdam. With it we carried out investigations on amino acids, resins and dyestuffs.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Modern liquid chromatography is a powerful, versatile separation technique. One can choose from four different separation modes. Liquid-solid: liquid-solid chromatography is adsorption chromatography.

Ion-exchange: ion-exchange chromatography separates ions on the basis of their relative affinity for an ion-exchange resin.

Liquid-liquid: liquid-liquid chromatography separates molecules on the basis of their differential solubility in two immiscible liquids; one moving, the other stationary.

Steric exclusion: In steric exclusion chromatography, compounds are separated according to their molecular size.

The performance of HPLC is in the most favourable case 300 to 400 times better than that of thin-layer chromatography, thin-layer chromatography having 1000-1500, liquid chromatography 40000 plates per meter. Accordingly it is possible to work quantitatively with a very small sample.

In the analysis of animal glues, which as mentioned before often differ in concentration of the various amino acids, it would be possible by this method to distinguish between skin-glue and bone-glue and between egg-white and egg-yolk. In the wake of experimental work we may conclude that for the analysis of animal glues as well as for gums and probably also for dyestuffs and resins HPLC appears to be most promising.

DESCRIPTION OF THE APPARATUS (6)

Liquid chromatography can be used for a much broader range of analyses than gas chromatography. A special apparatus exists for liquid chromatography; it provides the highest possible perfor-

mance. For our experiments we had at our disposal a Varian Aero-graph Model 8500 liquid chromatograph, with a high pressure pump, flow controller and pressure monitor. This apparatus was combined with a Varian Techtron 635 UV-Visible Spectrophotometer, a direct reading double beam instrument that can also be used in the single beam mode with a wavelength range between 180 and 850 nm and also with a recorder.

Some specifications of the model 8500 are:

The high pressure pump has a maximum flow rate of 990 ml/hr over the complete range and a maximum pressure of 8500 psi (600atm).

The Varian liquid chromatography injector is constructed of stainless steel and teflon.

The septum injector has a maximum pressure of 1000 psi (70 atm).

Columns: We used one 8500 psi MicroPak column SI 60-10 and one 8500 psi MicroPak column CN.

Variscan UV-Vis detector: Cell Design: Dual waterjacketed micro-volume flow cells. Cell Volume: 8 microliters.

1 mm x 10 mm. Maximum Cell Pressure: 500 psi.

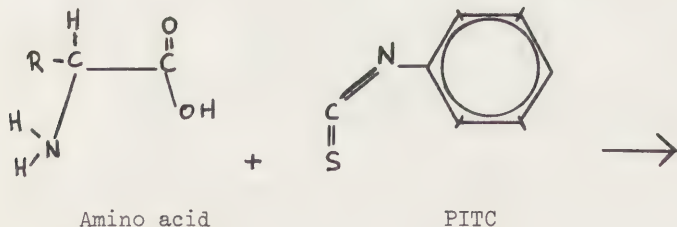
EXPERIMENTS

Animal glues: The glues, containing proteins, are hydrolysed into amino acids (3,5).

Method of hydrolysis (7): The sample is put into a small glass tube. About five drops of 0,3 N hydrochloric acid are added. The glass tube is shut off from air by melting the top of the glass tube. Then it is placed into an oven with a temperature of 105°C. for about 16 hours. After hydrolysis the sample is evaporated to dryness. For the separation with HPLC the amino acids are transformed into PTH amino acids.

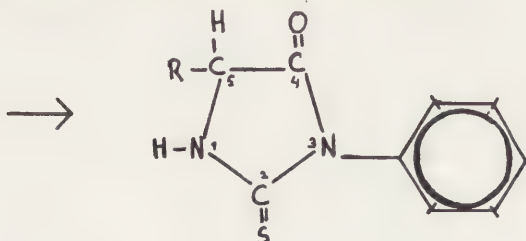
PREPARATION OF PTH AMINO ACIDS FOR LIQUID CHROMATOGRAPHY (2)

For liquid-chromatographical separation of amino acids the compounds are best transformed into the 3-phenyl-2-thiohydantoin derivatives by means of phenylisothiocyanate (C_6H_5NCS).



75/15/5-4

3-phenyl-2-thiohydantoin amino acid.



The addition of C (labelled 2) to N (labelled 1) takes place in basic solution (pH=10,1).

The closure of the five-membered ring between atoms 3 and 4 occurs in acid medium (pH=1).

PROCEDURE

The procedure of the microsynthesis after Sjöquist was followed, as quoted by G. Pataki (2).

Small deviations were as follows: not 0,5 μ M amino acid was prepared, but 100 μ g, about twice as much.

Instead of triethylamine, trimethylamine was used, the pH of the buffer solutions was measured as 10,2.

The drying was done in a vacuum desiccator over KOH pills and P₂O₅ powder.

The acid solution was prepared by mixing 1 part HCl (30%), 2 parts H₂O (distilled) and 3 parts acetic acid (99%).

The residue was taken up in 400 μ l of dichloromethane and volumes of 1 to 5 μ l were injected.

Reference amino acids were from BDH. Chemicals Ltd., Poole, England. PTH derivatives were prepared of glycine, alanine, proline, hydroxyproline, aspartic acid, glutamic acid, arginine mono HCl, lysine HCl (being the major components of collagen) and leucine, isoleucine, valine, β -phenylalanine (belonging to a test mixture of which the chromatographical separation has been published by the supplier of the apparatus, Varian).

A number of actual hydrolysates of samples and raw materials was prepared according to the same procedure. Quantities of samples were estimated to yield amounts of PTH derivatives per compound, comparable to the amounts of the pure amino acids which were prepared.

Derivatives of aspartic acid and glutamic acid were not found in the chromatograms, as was to be expected. Pataki (2) mentions special procedures for their synthesis. Also the arginine derivative did not show up.

RESULTS

The identification of glues, separated as PTH amino acids:
The first step in our research was to chromatograph the chemically pure amino acids which were transformed into PTH amino acids.
Conditions: Column 25 cm x 2 mm i.d.; MicroPak SI 60-10; Eluent CH_2Cl_2 ;

Flow rate 120 ml/hr.; 2000 psi; Detector UV 254 nm. The injection was 1 μl (about 1 μg). The results are found in Fig. 1.

Fig. 2: Equal quantities of seven PTH amino acids are mixed. From this mixture 10 μl (about 10 μg) is injected.

Fig. 3A: A sample of the notebook of A. v.d. Werff, a Dutch painter of the second part of the seventeenth century is hydrolysed and transformed into PTH amino acids.

Fig. 3B: Pure caseine is hydrolysed and transformed into PTH amino acids. The injection is in both cases 8 μl (about 8 μg).

Comparison between figure 3A and 3B shows that the binding medium of the notebook consists of caseine.

Figs. 4A and 4B: Samples of bone glue are hydrolysed and respectively one hour and sixteen hours. The injection is 10 μl (about 10 μg). The chromatograms show clearly the difference of the method of hydrolysis. More research should be done to find the best time of hydrolysis.

Fig. 5A: Pure skin glue is hydrolysed and transformed into PTH amino acids. The injection is 6 μl (about 6 μg).

Fig. 5B: A sample of a seventeenth century Flemish painting: "Farmers' -scene" has been taken to analyse the binding medium. The sample is hydrolysed and transformed into PTH amino acids.

Figs. 6A and 6B: Egg-white and a whole egg (egg-white and egg-yolk) are hydrolysed and transformed into PTH amino acids. The injection is in both cases 8 μl (about 8 μg).

Comparison between the two chromatograms shows that it is possible to distinguish egg-white and egg-yolk from each other through the different concentration of the same amino acids. Our research has been carried out on a MicroPak SI 60-10. According to Varian (6) better separation of the PTH amino acids is possible on a MicroPak SI-10. (Fig. 8). It is also possible to work on a MicroPak CN-10, where the mobile phase is a gradient as indicated in figure 9.

Note: The unnumbered peaks represent the reagent.

Fig. 8

PTH Amino Acids

CONDITIONS:

Column: MicroPak SI-10.

50 cm x 2 mm i.d.

Mobile Phase: Dichloromethane.

Flow Rate: 2 ml/min.

Pressure: 2000 psi.

Detector: Varian UV 254 nm at

0.64 a.u.

Sample: Phenylthiohydantoin

amino acids:

1. Proline
2. Leucine
3. Isoleucine
4. Valine
5. Phenylalanine
6. Methionine



75/15/5-6

RESINS, DYESTUFFS AND GUMS:

Resins: (4)

Sandarac, Venice turpentine; shellac; dammar; elemi; mastic; colophony; copal.

Column:

MicroPak SI 60-10

MicroPak CN

Flow rate:

10 ml/hr.; 30 ml/hr.; 60 ml/hr.; 120 ml/hr.

Detector U.V.:

241 nm

Mobile Phase:

Hexane/heptane

Methylenechloride (CH_2Cl_2)

CH_2Cl_2 /hexane/isopropyl alcohol (IPA)

Ethanol/heptane

Ethanol

Results:

Using the column SI 60-10 and mobile phase of ethanol/heptane (3:1), we had a good separation of a mixture of three resins i.e. mastic, colophony and shellac. In our case the detection limit is 1 $\mu\text{g}/\mu\text{l}$. The detection wavelength for all resins was 241 nm. We are sure that, if we had the right column, the right mobile phase and the right flow, we could attain much better results.

Natural Dyestuffs:

alizarin; purpurin; quercetin; rhamnetin; fisetin; maclurin; bixin; kaempferol; crocetin; morin; quercetin.

Column:

MicroPak SI 60-10

MicroPak CN

Flow rate:

60 ml/hr.; 120 ml/hr.

Detector U.V.:

310 nm; 257,5 nm.

Mobile Phase:

Ethylacetate (Etac.) Ethanol/heptane; Chloroform/methanol; Ethanol

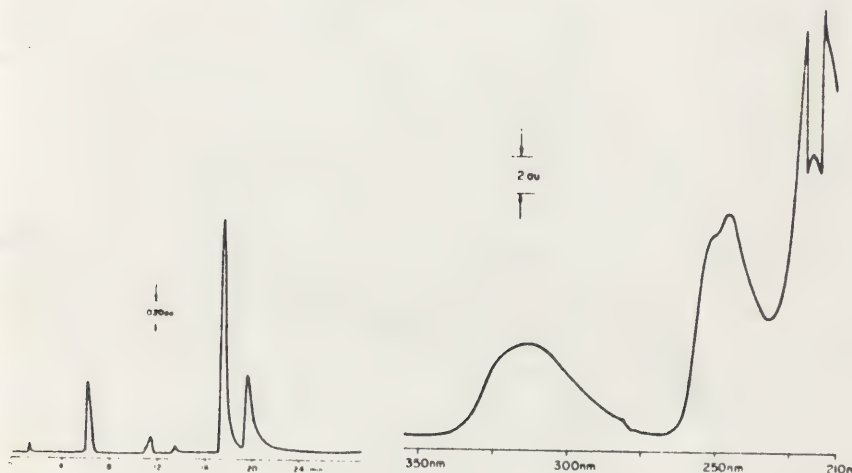
Iso-propyl alcohol (IPA)/Methylenechloride (CH_2Cl_2)

IPA/Etac.

Results:

Quercetin, maclurin and alizarin gave in our experiments a good result. For all the other dyestuffs our standard conditions were not suitable. The method which Varian (6) developed makes it possible to separate flavonones of plants (Fig. 10). This method may be useful in the analysis of yellow dyestuffs containing flavonoids.

Figure 10: Plant Flavonones. Conditions: MicroPak Column 0.24 x 50 cm. Eluent: gradient from hexanes to 90/10 dichloromethane/isopropanol.

Gums:

Binding materials like arabic gum have to be hydrolysed in sugars (8). We had no time to do experiments, but Varian was kind enough to give us the data of their application laboratory in Switzerland. The results can be seen in Fig. 7.

CONCLUSION

From our experiments which were carried out in a very short time we can conclude that the HPLC is a very promising technique for the analysis of binding media, especially animal glues. We are quite hopeful that through this method it will be possible to identify the various glues.

ACKNOWLEDGEMENT

The author is much indebted to the firm Varian Benelux b.v., Amsterdam, (especially to Mr. H. Visser, marketing engineer), for giving us on loan for one month their complete HPLC-equipment and for allowing us to use all their relevant data. The practical part of our experiment could not have been done in such a short time without the help of Miss Thea B. van Oosten. Appreciation also goes to Mr. J.A. Mosk for his help in preparing the PTH amino acids. Mrs. Judith Hofenk de Graaff gave stimulating assistance throughout the work.

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 8. Siemens, "Analysentechnische Mitteilungen nr. 85:
 - 1) Verteilungs-chromatographie von PTH-Aminosäuren, PTH-Leucin neben Isoleucin;
 - 2) Verteilungs-chromatographie von PTH-Aminosäuren, hydrophobe Gruppe;
 - 3) Verteilungs-chromatographie von PTH-Aminosäuren, hydrophile Gruppe;
 - 4) Ionenaustausch-chromatographie von Zuckern nach Floridi;
 - 5) Ionenaustausch-chromatographie von Zuckern nach Samuelson.
-

A B S T R A C T

For the analysis of binding media various methods of spectrometry and chromatography can be used. However, for the analysis of animal glues these methods do not give always satisfactory results. High performance liquid chromatography (HPLC) seems to be potentially more promising due to a higher resolution.

Experimental work was done with equipment of the firm Varian Benelux b.v., Amsterdam.

Amino acids can be separated as PTH amino acids and through this separation it is possible to distinguish egg-white from egg-yolk. More experiments will be done on resins, gums and dyestuffs.

Figure 1:

CONDITION:

Column 25 cm x 2 mm I.D.
 MicroPak SI 60-10
 Mobile Phase: CH_2Cl_2
 Flow rate: 120 ml/hr.
 2000 PSI
 Detector U.V.: 254 nm.

- | | | | | | | | | | |
|------------|------------|-----------------|-----------|---------------------------|------------|------------|-----------|-------------------|------------|
| 1. Proline | 2. Leucine | 2A. ISO-Leucine | 3. Valine | 4. β -Phenylalanine | 5. Alanine | 6. Glycine | 7. Lysine | 8. Hydroxyproline | X. Reagent |
|------------|------------|-----------------|-----------|---------------------------|------------|------------|-----------|-------------------|------------|

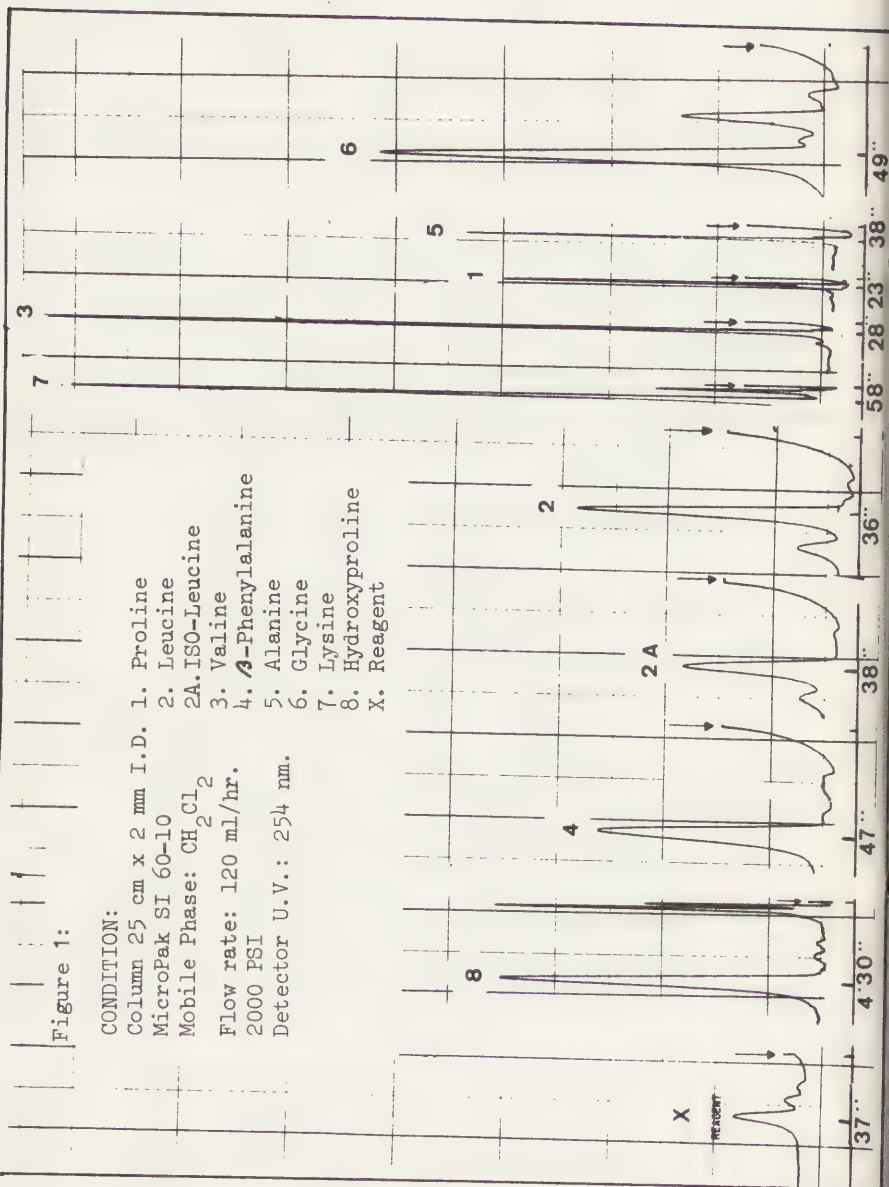


Figure 2:

Mixture of pure PTH Amino acids

CONDITION:

Column 25 cm x 2 mm I.D.

MicroPak SI 60-10

Mobile Phase: CH_2Cl_2
(not present)

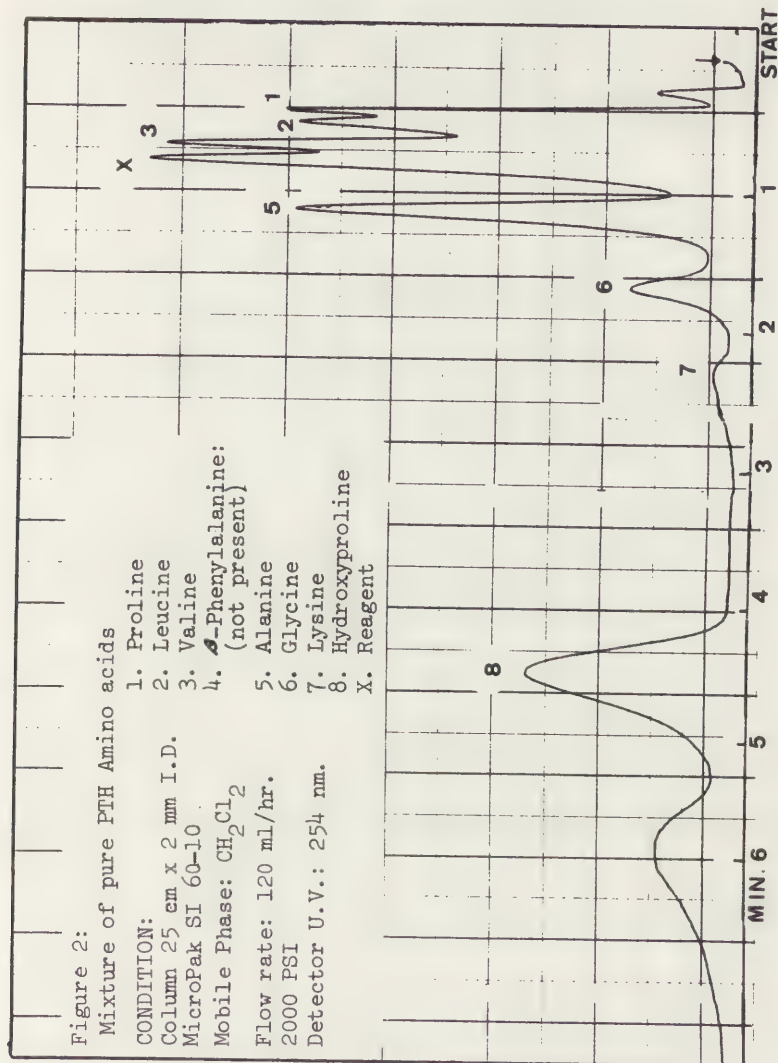
Flow rate: 120 ml/hr.

2000 PSI

Detector U.V.: 254 nm.

1. Proline
2. Leucine
3. Valine
4. β -Phenylalanine:
5. Alanine
6. Glycine
7. Lysine
8. Hydroxyproline

X. Reagent



75/15/5-12

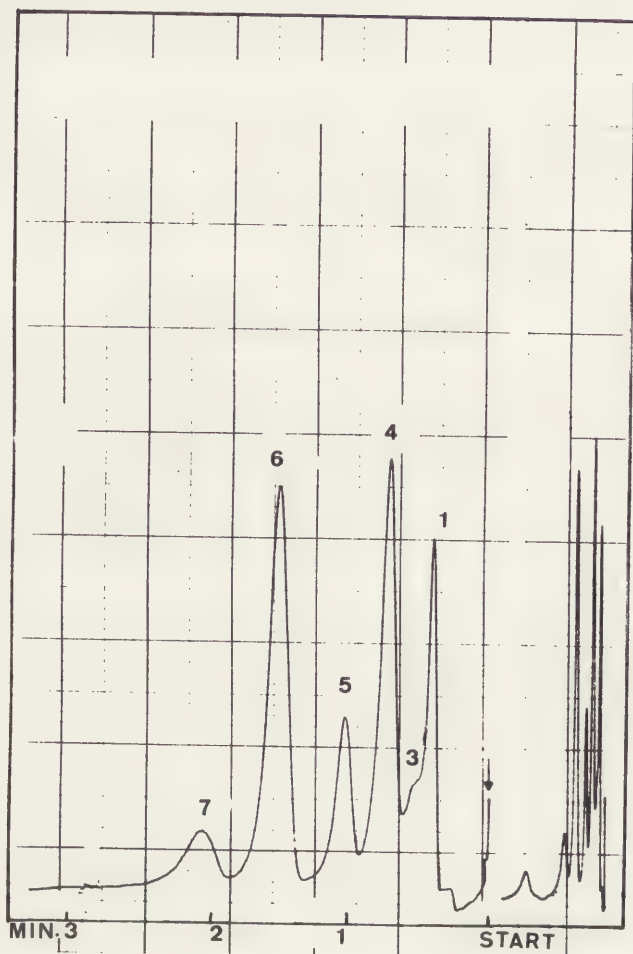


Figure 3A: Sample:
Notebook of A. v.d. Werff. Second part of 17th. cent.

CONDITION:

Column 25 cm x 2 mm I.D.

MicroPak SI 60-10

Mobile Phase: CH_2Cl_2

Flow rate: 120 ml/hr.

2000 PSI

Detector UV: 254 nm.

1. Proline
2. Leucine: not present
3. Valine
4. β -Phenylalanine
5. Alanine
6. Glycine
7. Lysine

Figure 3B

Caseine

CONDITION:

Column 25 cm x 2 mm I.D.

MicroPak SI 60-10

Mobile Phase: CH_2Cl_2

Flow rate: 120 ml/hr

2000 PSI

Detector UV: 254 nm.

1. Proline

2. Leucine

3. Valine

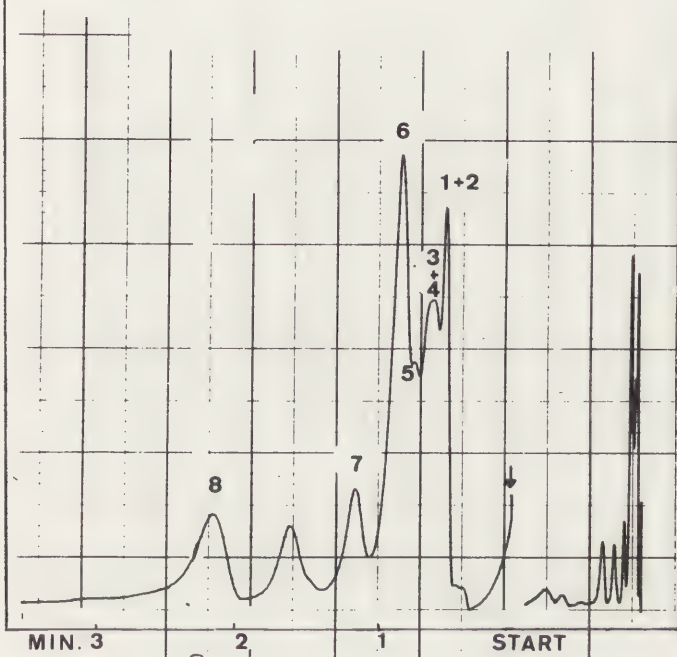
4. β -Phenylalanine

5. Alanine

6. Glycine

7. Lysine

8. Hydroxyproline



In both figures 3A and 3B time scales are different because of different instrument operation.

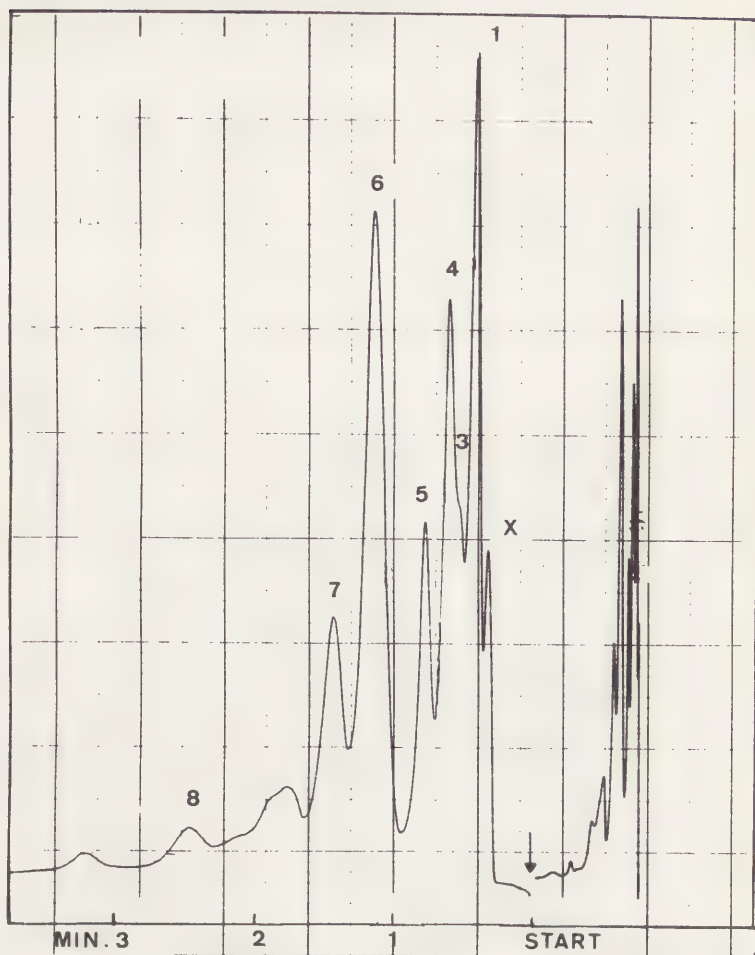


Figure 4A
Bone glue 1 hour hydrolysed

CONDITION:

Column 25 cm x 2 mm I.D.

MicroPak SI 60-10

Mobile Phase: CH_2Cl_2

Flow rate: 120 ml/hr.

2000 PSI

Detector UV: 254 nm

1. Proline
2. Leucine: not present
3. Valine
4. β -Phenylalanine
5. Alanine
6. Glycine
7. Lysine
8. Hydroxyproline
- X. Reagent

75/15/5-15

Figure 4B

Bone glue 16 hours hydrolysed

CONDITION:

Column 25 cm x 2 mm I.D.

MicroPak SI 60-10

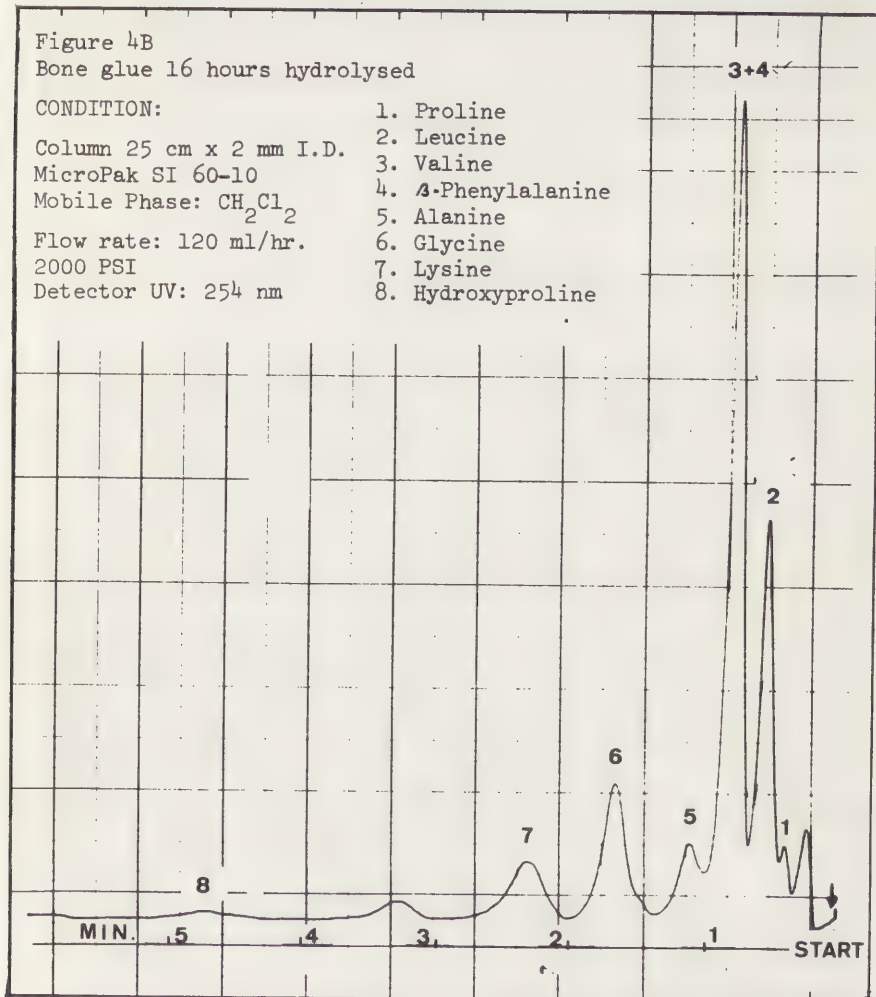
Mobile Phase: CH_2Cl_2

Flow rate: 120 ml/hr.

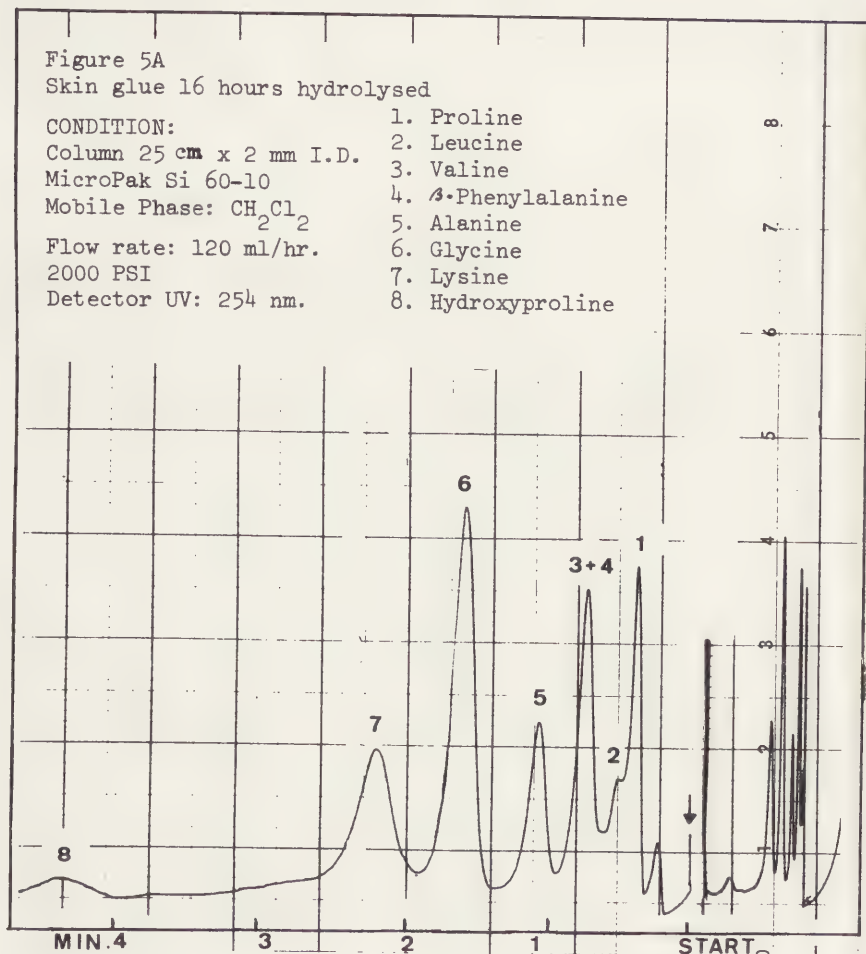
2000 PSI

Detector UV: 254 nm

1. Proline
2. Leucine
3. Valine
4. β -Phenylalanine
5. Alanine
6. Glycine
7. Lysine
8. Hydroxyproline



75/15/5-16



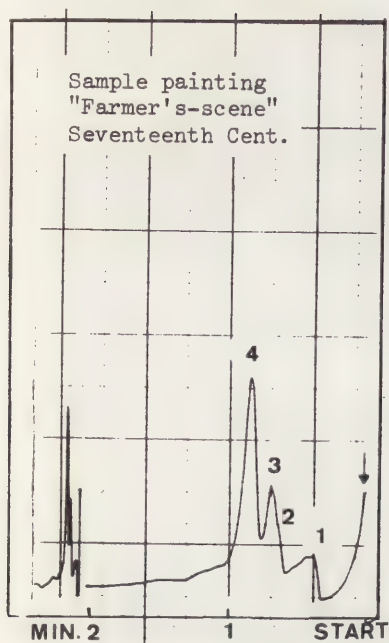


Figure 5B:

CONDITION

Column 25 cm x 2 mm I.D.
MicroPak SI 60-10
Mobile Phase: CH_2Cl_2
Flow rate: 120 ml/hr.
2000 PSI
Detector UV: 254 nm.

1. Proline
2. Leucine
3. Valine
4. β -Phenylalanine

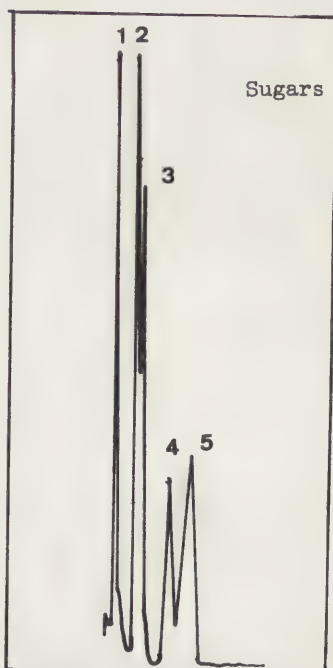


Figure 7:

CONDITION

Column 25 cm x 2,2 mm
MicroPak NH_2
Mobile Phase: $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ 12/88
Flow rate: 60 ml/hr.
700 PSI
Detector: R.I.
Record Speed: 0,2 cm/min.

1. Alcohol
2. Fructose
3. Glucose
4. Saccharose
5. Maltose

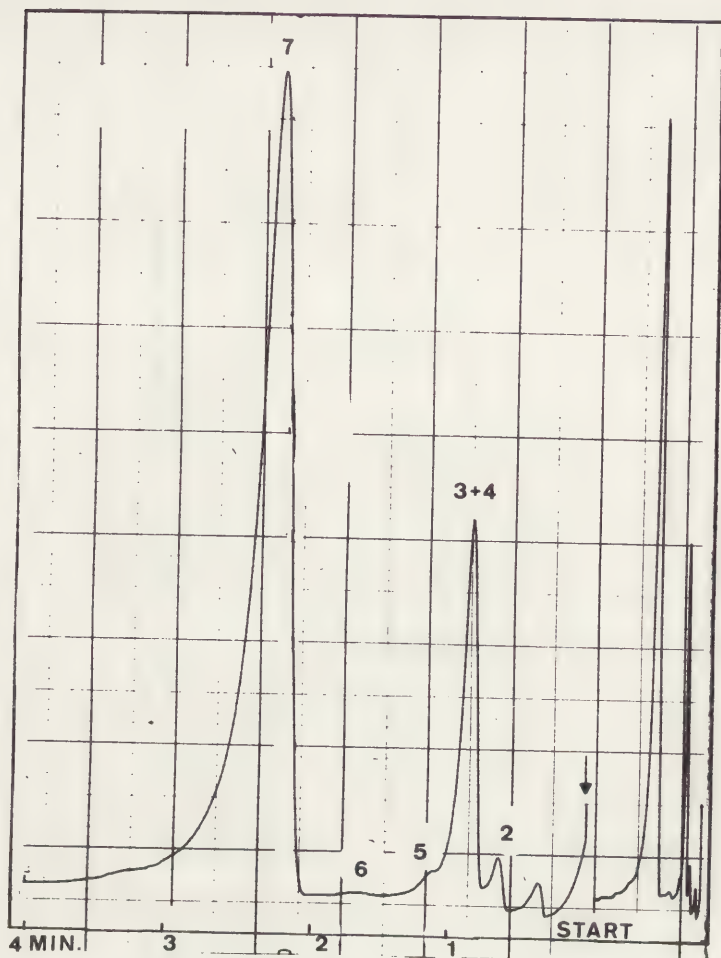


Figure 6A:
Eggwhite 16 hours hydrolysed

CONDITION:

Column 25 cm x 2 mm I.D.
MicroPak SI 60-10
Mobile Phase: CH_2Cl_2
Flow rate: 120 ml/hr
2000 PSI
Detector UV: 254 nm.

1. Proline: not present
2. Leucine
3. Valine
4. β -Phenylalanine
5. Alanine
6. Glycine
7. Lysine

75/15/5-19

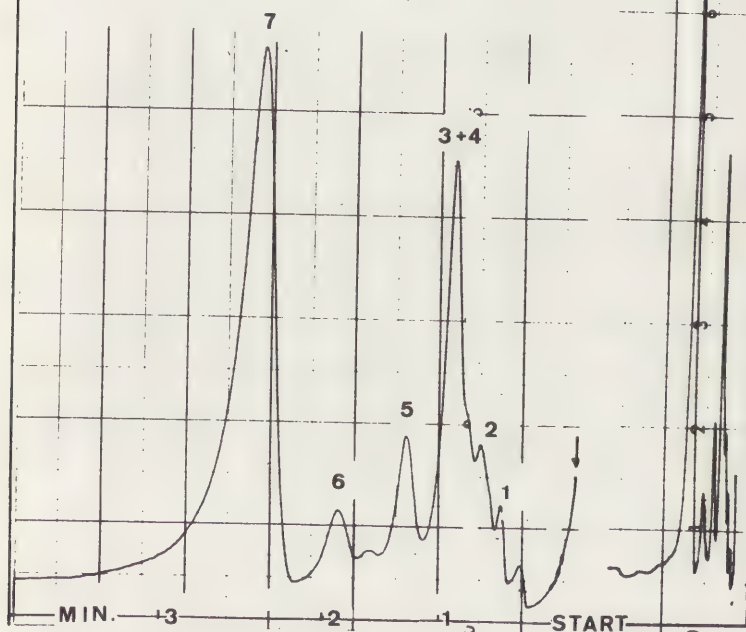
Figure 6B

Eggwhite and egg-yolk 16 hours hydrolysed

CONDITION:

Column 25 cm x 2 mm I.D.
MicroPak SI 60-10
Mobile Phase: CH_2Cl_2
Flow rate: 120 ml/hr.
2000 PSI
Detector UV: 254 nm.

1. Proline
2. Leucine
3. Valine
4. β -Phenylalanine
5. Alanine
6. Glycine
7. Lysine



75/15/5-20

Fig. 9

PTH Amino Acids

CONDITIONS:

Column: MicroPak CN-10,
25 cm x 2 mm i.d.

Mobile Phase: Gradient as indicated
from hexanes plus 0.1% isopro-
panol to 88% hexanes; 6% isopro-
panol, 6% dichloromethane.

Flow Rate: As indicated.

Pressure: As indicated.

Detector: Varian UV 254 nm at
0.64a.u.s.

Sample: PTH amino acids:

1. Leucine
2. Valine
3. Phenylalanine
4. Alanine
5. Glycine
6. Threonine
7. Tryptophan
8. Tyrosine

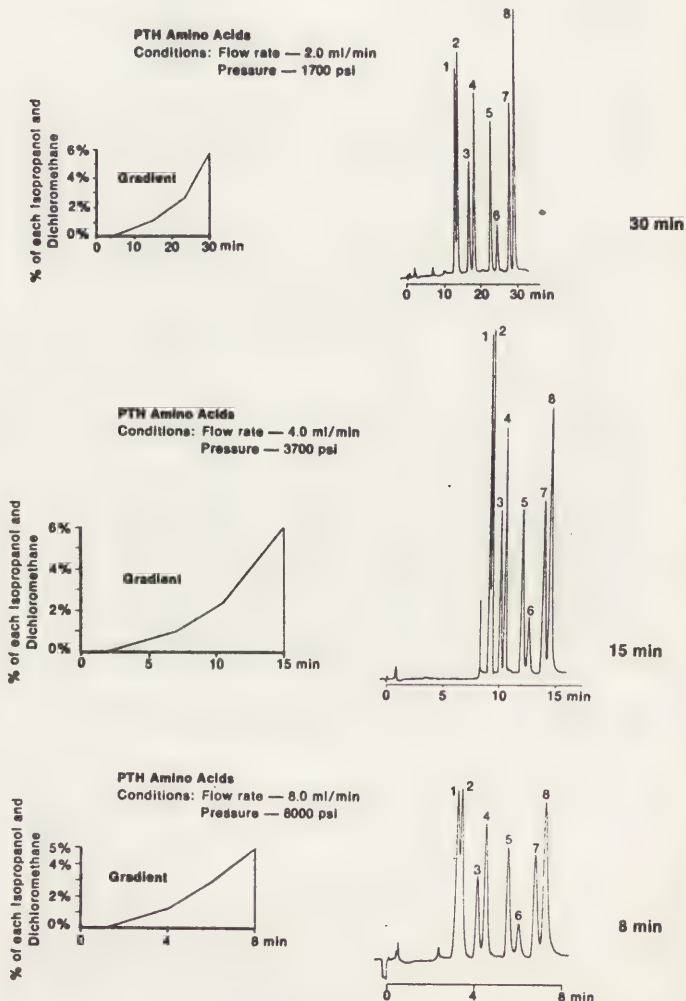


TABLE XI

COLD EXTRACTION pH FOR PAPER-POLY(VINYL ACETATE) EMULSION SYSTEMS^a

AGED AT 95°C AND <10% RH

Aging Time Days	Adhesive	Airflex 400	Booksaver	Elmer's Glue All	Elvace 1874	Everflex A	Everflex G	Flexbond 800	Jade 403	Untreated Paper
0		5.9	5.8	4.6	5.4	6.2	6.2	6.0	6.2	6.2
1		6.0	6.4	6.2	6.1	6.2	6.3	6.0	6.2	6.1
5		5.9	6.2	6.0	6.2	6.0	6.2	6.0	6.1	5.5
9		6.0	6.8	6.8	6.5	6.8	6.8	6.7	5.9	6.4
16		6.2	6.4	6.2	6.0	6.0	6.2	6.2	6.0	6.0

^a Cold extraction on 1 gram paper-adhesive system to 70 ml H₂O after one hour.

TABLE XII

SOLUBILITY IN WATER AND TOLUENE OF ADHESIVES AGED AT 95°C AND <10% RH

Adhesive	Airflex 400	Booksaver	Elmer's Glue All	Elvace 1874	Everflex A	Everflex G	Flexbond 800	Jade 403									
Aging Time Days	Hours in Solvent	W ^a	T	W	T	W	T	W	T	W	T	W	T	W	T		
0	(1)	5	2	5	5	4	2-3	5	4-5	3-5	2-4	5	2-4	5	6	4	3-5
	(2)	5	3-4	5	5	4	2-3	5	4	5	4	5	2	5	6	4	N.D. ^b
	(24)	5	4	5	4-5	4	4	5	5	5	4	5	4	5	6	5-6	4
1	(1)	5	4	5	4	2-3	2	5	4	5	4	5	4	5	4	5	4
	(2)	5	4	5	4	2-3	3	5	3-4	5	4	5	4	5	4	5	3-4
	(24)	5	4	5	2-4	5	2-4	5	4	5	2-4	5	4	5	2-4	5	4
5	(1)	5	4	5	4	5	3	5	2-4	5	4	5	4	5	4	5	4
	(2)	5	4	5	2-4	5	2-4	5	4	5	4	5	4	5	4	5	2-4
	(24)	5	4	5	2-4	5	2-4	5	4	5	4	5	4	5	4	5	2-4
9	(1)	3-5	4	3	2	3-5	2	5	4	5	4	5	4	5	4	5	2
	(2)	5	4	3	2	3-5	2	5	4	5	4	5	4	5	4	5	2
	(24)	5	2-4	3-5	4	5	2	5	4	5	4	5	4	5	4	5	2-4
16	(1)	5	4	3-5	4	3-5	4	5	4	5	4	5	4	5	4	3-5	2-4
	(2)	5	2	3-5	4	5	2	5	4	5	4	5	4	5	4	3-5	4
	(24)	5	4	3-5	4	5	2	5	4	5	4	5	4	5	4	3-5	2-4

Solubility Key

1. No change at all.
2. Gel-like but adherent on contact with a glass rod.
3. Dislodges only at point of contact.
4. Gel-like but breaks up on contact with a glass rod.
5. Layer peels off fairly easily on contact with a glass rod.
6. Soluble.

^a W denotes water; T denotes toluene^b N.D. denotes no data



IDENTIFICATION DES CUIRS ET PARCHEMINS ANCIENS À L'AIDE DU MICROSCOPE

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ABSTRACT

To identify the animal origin of leather or parchment, samples of 2 or 3 square mm, are embedded in paraffin wax (melting point 54-56°C) after they have been softened. Then, horizontal and vertical sections of 5 to 10 μ are made. After coloration, they are examined under a microscope with low magnification, x 40 or x 100. Identification is made possible by hair follicles which form the grain pattern. The microscopic examination of horizontal sections permits the observation of the follicular arrangement which is characteristic of animal species. An examination of cross sections provides additional information about the length of these follicles and the angle which they form with the skin surface. The compiling of a catalogue of ancient and modern leathers and parchments in various states of preservation has been undertaken. Each histological preparation brings on a color microphotograph which is classified. This preliminary work is necessary for the identification of an unknown material.

Des prélèvements de cuir ou de parchemin dont l'origine animale est à identifier, de 2 ou 3 mm² de surface, sont inclus dans la paraffine 54-56°C, après avoir été assouplis. Ils sont ensuite coupés parallèlement et perpendiculairement à la surface de la peau, à une épaisseur de 5 à 10 μ . Après coloration, ils sont examinés au microscope à faible grossissement, x 40 ou x 100. L'identification est possible grâce aux follicules pileux dont la disposition forme le dessin du grain. L'examen en coupe parallèle permet d'observer l'arrangement folliculaire, caractéristique de l'espèce animale. L'examen en coupe transversale apporte des informations complémentaires sur la longueur de ces follicules et l'angle qu'ils forment avec la surface de la peau. La constitution d'un catalogue de cuirs et parchemins anciens et modernes dans différents états de conservation a été entreprise. Chaque préparation histologique donne lieu à une microphotographie en couleur, classée et répertoriée. Ce travail préliminaire est indispensable à l'identification d'un matériel inconnu.

Le problème de l'identification des cuirs et parchemins anciens a depuis longtemps préoccupé restaurateurs et historiens. Il n'est pas toujours possible en effet, même pour un oeil averti, de pouvoir identifier un cuir vieilli, dont l'aspect s'est beaucoup modifié au cours du temps. Encore plus difficile est parfois l'identification d'un parchemin. L'examen sous le microscope pourra apporter dans certains cas une aide précieuse.

Le cuir et le parchemin ont la même origine : la peau d'un animal. Ils sont fabriqués à partir du derme ; celui-ci est formé de deux couches, la couche papillaire ou "fleur" dans laquelle les faisceaux de collagène forment un réseau assez fin, et la couche réticulaire, plus profonde, encore appelée "chair", où les faisceaux de collagène sont en réseaux plus épais. C'est dans la couche papillaire que sont situés les follicules pileux et les glandes de la peau (sudoripare et sébacée), qui se développent à partir de l'épiderme. On rencontre également des fibres élastiques entre les faisceaux de collagène et autour des follicules et des glandes.

Les différentes opérations menées par le tanneur et le parcheminier visent à éliminer l'épiderme et la couche sous-cutanée ou hypoderme. Il ne restera pratiquement que les fibres de collagène contenues dans le derme, qui, par réaction chimique avec le tannin donnent le cuir ; le parchemin, lui, n'est pas tanné. La transformation de la peau en cuir modifie peu la structure du derme. On retrouve à peu près intacts les faisceaux de collagène. Il n'en est pas de même avec le parchemin (4), car au cours de sa préparation, la structure du derme subit de grandes altérations. Le fait d'étirer les peaux encore mouillées, lors de leur séchage sur cadres, tend à modifier la disposition des fibres. Au lieu d'être entrelacées, elles se disposent en couches lamellaires, parallèlement à la surface de la peau. C'est probablement la raison pour laquelle le parchemin peut être aussi facilement dédoublé. Une autre modification de sa structure est due au fait que la peau, alors qu'elle est encore sur cadres, est polie et adoucie à l'aide de pierre ponce, ce qui a pour effet de l'amincir. Ainsi une coupe transversale dans un parchemin ne donne plus l'image des deux couches du derme "grair" et "chair" comme on peut les voir dans une coupe de cuir.

La méthode classique de préparation des cuirs pour l'examen au microscope est la congélation : les échantillons, après avoir été imbibés d'eau pendant plusieurs heures, sont congelés grâce à une détente de gaz carbonique. Nous n'avons pas retenu cette méthode qui s'est révélée inutilisable pour certains cuirs anciens très abîmés qui se décomposent rapidement quand on les met dans l'eau. Nous avons préféré l'inclusion dans la paraffine. Les échantillons de cuir et de parchemin, de quelques mm² de surface, sont d'abord assouplis dans le mélange alcool-formol-carbonate de sodium en solution aqueuse (voir annexe 1) (6-9). Cette opération est très importante car il faut que les peaux soient suffisamment assouplies pour obtenir de bonnes préparations. Après déshydratation, les échantillons sont imprégnés à l'aide d'un bain de paraffine 54-56°C.

L'imprégnation doit être rapide, pour éviter un durcissement des tissus ; aussi est-elle faite sous vide, ce qui en diminue considérablement le temps (6). Après inclusion dans la paraffine, des coupes de 5 à 10 μ d'épaisseur sont effectuées, parallèlement et perpendiculairement à la surface de la peau ; ces coupes sont ensuite colorées (voir annexe 2) et examinées à faible grossissement, x 40 ou x 100.

L'identification de l'espèce animale à laquelle appartient le cuir ou le parchemin peut se faire grâce à certains éléments et en particulier par la disposition des follicules pileux qui forme le dessin du grain. La coupe parallèle à la surface de la peau permet d'observer cet arrangement folliculaire. L'étude du développement des follicules de la peau a depuis longtemps préoccupé les biologistes. Il fut démontré vers 1920 que certains mammifères possèdent deux types de follicules pileux : les "primaires" et les "secondaires" (2-3-10). Les follicules primaires, généralement les plus grands, sont les premiers à être différenciés dans le fœtus ; ils sont connectés avec un muscle érecteur et une glande sudoripare. Les générations suivantes les follicules secondaires, se développent dans les espaces laissés entre les primaires et manquent généralement de muscle érecteur et de glande sudoripare (1-8). L'association en trio de primaires avec entre eux les secondaires constitue le groupement folliculaire unitaire. Cette disposition en trios peut déjà renseigner sur l'espèce, la peau de veau par exemple, n'ayant qu'un seul type de follicules : les primaires, disposés au hasard. Le diamètre des follicules, le rapport de nombre entre secondaires et primaires et la disposition des uns par rapport aux autres (5) sont aussi des facteurs très importants.

Les follicules pileux peuvent également être observés en coupe transversale : l'implantation plus ou moins profonde du poil dans le derme, la régularité de l'angle formé par le follicule pileux et la surface de la peau, ainsi que le rapport d'épaisseur entre les couches papillaire et réticulaire sont des critères d'identification. Ainsi la chèvre a des poils profondément implantés, de façon très parallèle et très régulière ; tandis que le mouton a des poils irrégulièrement implantés et beaucoup moins profondément ; de plus, la couche papillaire, par rapport à la couche réticulaire, est beaucoup plus fine chez le mouton que chez la chèvre.

Il est parfois difficile d'établir une identification. La disposition des follicules dans la peau de mouton s'est beaucoup modifiée depuis le mouton sauvage jusqu'aux races modernes ; l'évolution va en particulier dans le sens d'une diminution des follicules primaires, les races modernes étant constituées de plusieurs maillons de cette évolution (7). Il se trouve que l'arrangement folliculaire de la peau de chèvre est très proche de celui d'un certain type de mouton (5). Dans ce cas, seul l'examen attentif de tous les autres critères mentionnés plus haut, pourra permettre une identification.

Nous avons donc entrepris la constitution d'un catalogue de différents cuirs et parchemins dont l'espèce animale est connue. Les échantillons proviennent soit de peaux neuves, soit de reliures ou de

manuscripts anciens dans différents états de conservation. Chaque préparation histologique donne lieu à une microphotographie en couleur, classée et répertoriée. Nous voulons établir ainsi un grand fichier de références qui sera un guide indispensable pour l'identification d'un matériel inconnu.

L'examen microscopique des cuirs et des parchemins est une bonne méthode pour leur identification, à condition toutefois d'y retrouver les éléments nécessaires. C'est ainsi qu'il sera impossible de déterminer la nature d'un cuir abîmé dont le grain a disparu par usure, ou d'un parchemin qui serait préparé avec la couche profonde du derme. Mais, si le prélèvement à partir duquel est réalisée l'analyse, contient quelques restes folliculaires en bon état de conservation, son origine animale pourra être déterminée grâce au microscope.

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Conservation des Documents Graphiques
Paris

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ANNEXE N° 1PREPARATION DU REACTIF ASSOUPLEISSANT

Ethanol 96°	=	30 volumes
Formol phosphaté*	=	50 "
CO ₃ Na ₂ en solution aqueuse à 5 %	=	20 "

* Formol phosphaté :

Na H ₂ PO ₄ , H ₂ O	=	4,00 g.
Na ₂ H PO ₄ , anhydre	=	6,50 g.
eau distillée	=	900 ml
formol (solution commerciale à 40 %)	=	100 ml

Si le cuir est très abîmé, le formol phosphaté peut être légèrement modifié en remplaçant 200 ml d'eau par 200 ml d'alcool à 96°. Le degré alcoolique du mélange étant ainsi augmenté, le cuir risque moins de se décomposer.

Le temps de séjour dans le mélange est très variable ; il est à déterminer pour chaque échantillon ; 24 heures suffisent en général pour le cuir, plusieurs jours sont parfois nécessaires pour assouplir le parchemin. Des changements de liquide doivent être faits fréquemment.

COLORATION DES COUPES, d'après AUBER (1)

- Déparaffinage des coupes dans deux bains de xylène et hydratation par passage dans des bains successifs d'alcool absolu, d'alcool à 95° contenant 10 % de formol, d'alcool 50°.
- Coloration 15 minutes par l'hématoxyline de Weigert (a) et rinçage à l'eau courante 5 minutes
- Différenciation par l'alcool chlorhydrique (alcool absolu à 0,5 % d'acide chlorhydrique) pendant quelques secondes et rinçage à l'eau courante 1 minute
- Coloration par la fuchsine basique (1 % dans l'alcool 50°) 5 minutes et rinçage rapide à l'eau distillée
- Différenciation par l'alcool absolu contenant quelques gouttes d'une solution alcoolique saturée d'acide picrique, jusqu'à décoloration du fond (examiner au microscope)
- Rinçage rapide dans l'alcool absolu, puis hydratation
- Coloration par le picro-indigo-carmin (b) 1 à 2 minutes
- Différenciation par l'alcool 70° pendant 1 minute
- Déshydratation rapide par l'alcool 100%, puis le xylène et montage

Préparation des réactifs *a) Hématoxyline de Wiegert

préparée en mélangeant à parties égales :

- solution à 1 % d'hématoxyline dans l'alcool 96° (à partir d'une solution mère à 10 % préparée depuis plus de 6 mois)
- solution acide de chlorure ferrique : 1,16 g. de chlorure ferrique, 98 ml d'eau distillée, 1 ml d'acide chlorhydrique à 25 % (obtenu en ajoutant 100 ml HCl d = 1,19 à 50 ml eau distillée)

b) Picro-indigo-carmin

0,4 g. d'indigo-carmin dans 100 ml d'une solution aqueuse saturée d'acide picrique

* GABE (M.).- Techniques histologiques, Masson, Paris, 1968

RECENT EXPERIMENTS IN THE FIELD OF DISINFECTION OF BOOK MATERIALS

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In Italy the problem of the treatment of book materials on which the development of biological agents has taken place, either through accidental causes (floods in Florence of 4/11/66), or atmospheric causes, has assumed at times over the past few years imposing aspects and proportions.

Recently in the course of the transfer of the National Library of Rome from the old to the new premises, the opportunity to disinfect and disinfest a vast number of volumes emerged. These works which had been kept for a number of years in storerooms which were not in keeping with determined characteristics showed insect erosion and alterations of microbial origin.

It has therefore been necessary to examine from time to time methodologies which enabled the short term treatment in vacuum chambers or on the library premises, of the collections of damaged books, and to control by laboratory tests the results obtained. The rapidity of the interventions, especially in some cases proved to be indispensable to prevent the microbial agents from developing rapidly and damaging by their enzyme activity the paper, parchment and leather, and from provoking in serious cases alterations in structure.

The choice of chemical compounds to use for this purpose was made on the basis of experiments already carried out in other European countries, and after a careful and wide review of the literature on the subject. From the experimental and

bibliographical data collected, it seemed appropriate to use 3 fumigants: ethylene oxide, formaldehyde and methyl bromide (these last two were used both separately and in a mixture).

In this study the results of the following experiments will be synthetically reported:

- a) in vacuum chamber
- b) on the premises of the National Library of Rome
- c) in the Hall of the Angelica Library of Rome

TREATMENTS IN VACUUM CHAMBERS WITH ETHYLENE OXIDE

Ethylene oxide mixed with freon, in vacuum chambers has been widely used in Italy over the last few years for the treatment of books from the National Library of Florence damaged by the floods of 4/11/66 and more recently in an autoclave at the "Istituto di Patologia del Libro" of Rome.

Disinfection of flooded books of the National Library of Florence

A first experiment in the book field with ethylene oxide was made in Italy under emergency conditions at the National Library of Florence for the disinfection of about 1.200.000 volumes which had been affected by water and mud, and on which an ideal pabulum for microorganisms had been created. In this library at the proposal of specialists from the "Istituto di Patologia del Libro" an autoclave of 18m³ was set up in which about 2000 volumes were treated per day. A rapid preliminary experimentation was carried out to assess the efficacy of the gas in dosages of 160gr./m³ and 500 gr./m³, dosages which had also been used in France by Dott. Flieder and in Poland by Prof. Kowalik. This experiment enabled us to ascertain that the dosage of 160 gr./m³ was active only on some of the fungal species present on the flooded materials, and did not destroy the bacterial flora. The dosage of 500 gr./m³ on the other hand proved to be effective both on the bacterial forms and on most of the fungal forms.

Even though the results obtained in Florence were on the whole satisfying in that they enabled serious or merely incipient microbial attacks on books to be halted, such results however also brought to light the need to study the problem of disinfection with ethylene oxide in greater depth in order to

Treatments carried out with ethylene oxide

Dosage ethylene oxide	Temperature	Relative humidity	Duration in hours of treatments	Vacuum	Position of boxes	Percentage of samples on which ethylene oxide proved active
250 gr/m ³	25-35°C	50%	24	-	Open	97,5%
" "	" "	50-55%	48	-	"	100%
" "	" "	50-55%	72	-	"	95%
250 gr/m ³	25-30°C	50%	24	-	Closed	97,5%
" "	25-35°C	50-55%	48	-	"	100%
" "	" "	50-55%	72	-	"	97,5%
400 gr/m ³	30-35°C	50-60%	24	+	Open	92,5%
" "	25-35°C	65%	48	+	"	97,5%
" "	30-38°C	60-65%	72	+	"	97,5%
400 gr/m ³	30-35°C	45-50%	1,5	+	Closed	37,5%
" "	" "	50-60%	3	+	"	77,5%
" "	" "	" "	6	+	"	92,5%
" "	" "	" "	15	+	"	95%
" "	" "	40-60%	24	+	"	97,5%
" "	" "	50-55%	48	+	"	100%
" "	" "	50-65%	72	+	"	100%
500 gr/m ³	22°C	50-70%	24	+	Closed	100%
500 gr/m ³	30-35°C	45-54%	24	+	Closed	100%
700 gr/m ³	20°C	50%	24	+	Closed	92%
" "	30°C	50%	6	+	"	92%
" "	30°C	50%	24	+	"	96%
800 gr/m ³	30°C	50%	24	+	Closed	100%

Key: - The vacuum was not made before the introduction of gas
+ The vacuum was made before the introduction of gas

75/15/7-4

estimate the influence of the various parameters (temperature, humidity, dosages etc.) on the efficacy of the treatments.

Treatments in the disinfection vacuum chamber of the "Istituto di Patologia del Libro"

For about 2 years now the "Istituto di Patologia del Libro" has been equipped with a new vacuum chamber of 1.5 m³ in which it is possible to carry out fumigations with formaldehyde and ethylene oxide (the latter can be mixed with both freon and CO₂). In the interior of this chamber in which the atmospheric pressure 5 can be reached, it is possible to vary within wide limits the temperature and relative humidity. During treatments the books are placed on perforated shelves which allow the free circulation of the gas. In order to assess the efficacy of the ethylene oxide on the microorganisms of the paper, various tests were carried out varying certain parameters (dosages, duration of treatment). Furthermore, in order to estimate the penetration power of the fumigant, tests were carried out on samples placed both inside books open in a fan-like position, in which the gas penetrated easily, and inside books of a different format which were closed and compressed. (table 1)

Materials and methods

Samples

For the tests samples of paper which was severely damaged by microorganisms were used, which after the disinfection were washed in sterile distilled water to eliminate eventual spores present in the air introduced into the autoclave after the elimination of the gas, and then placed on agar saboraud and incubated for 14 days at 30°C.

Dosages

We carried out tests with dosages of ethylene oxide 250 -400-500-700-800 gr./m³. During the course of the experiments with 250 gr./m³, the vacuum was not made before the introduction of the gas. The aim of these experiments was to assess whether this dosage allowed the destruction of the fungal and bacterial flora present on the samples, if without the preliminary vacuum the gas penetrated between the pages of the books, and consequently if ethylene oxide

mixed with freon could be used for room treat-
ments.

Temperature, relative humidity and conditioning of books

The experiments were mainly carried out at temperatures between 20 and 30°C and 50-60% of relative humidity (table 1), temperatures at which the majority of the book microorganisms have quite an active metabolism. Before the introduction of the gas the books were left for 24 hours at the relative temperatures and humidity mentioned above. This device was used so that the book materials could reach an equilibrium with the atmospheric conditions, and so that consequently the necessary conditions could be created inside the books to obtain a more effective disinfectant action.

Results (table 1)

As can be seen from the table, with the dosage of 250 gr./m³ and times of 24-48 and 72 hours, the almost total destruction of the microbial agents on samples placed both in open and closed books was obtained.

The results obtained show that inspite of the fact that before the inlet of the gas, the vacuum was not made, ethylene oxide penetrated the books.

Particularly indicative are the data concerning tests carried out on samples disinfected with dosages of ethylene oxide of 400 gr./m³ and varying the duration of treatments from 1½-72 hours. These data clearly show the determining influence with the same dosages, exerted by the length of action of the gas. In fact while with 1½ hours the microorganisms were killed on 37,5% of the samples, this percentage increased in gradual and constant measure until it reached 100% with 48 hours of treatment.

Clearly positive results were also obtained with dosages of 500-600 and 800 gr./m³. It is interesting to note that during the course of our numerous experiments we have seen that if the mixture ethylene oxide-freon, a mixture which generally lasts 3 months, has not been prepared recently, its microbicidal activity is considerably weakened.

75/15/7-6

TREATMENT OF THE BOOK MATERIAL OF THE NATIONAL LIBRARY OF ROME

Among the numerous problems which have been faced in the course of the recent transfer of the Rome National Library from the old to the new premises, one problem in particular which is worthy of note is that concerning the dusting, disinfection and disinfestation of many ten thousands of books which showed alterations of biological origin. In 1971 when the organisation of transfer arrangements was underway, a Committee of experts was set up whose task was to examine along general lines, the state of conservation of the book material. Since it was necessary to produce in a short time significant data on possible attacks by insects and microorganisms, data which would permit the programming of disinfection and disinfestation operations, some members of this Committee investigated many rooms in the old premises in via del Collegio Romano and also in other premises situated in other areas of Rome, where ten thousands of books had been transferred from the ancient Library buildings after serious damage which had compromised the statics had taken place.

During these investigations to identify alterations of biological origin in the book collections, books from various parts of the storerooms were removed and in particular those books which had been arranged on shelves along damp walls or in parts of the premises which were badly ventilated, where atmospheric conditions which could encourage the development of insects and microorganisms existed.

Even though these examinations were not sufficient to be able to express a precise judgement on the extent and gravity of the damage, they did draw attention to indicative data on the existence of hot-beds of infection and infestation, the atmospheric conditions of book storerooms and the percentage of water contained in the books.

The data obtained during the course of these investigations were carefully examined and selected by the Committee who decided to treat the damaged books possibly in vacuum cells with the gaseous substances (ethyleneoxide, methyl bromide, and formaldehyde) commonly used to destroy biological agents which damage paper, parchment etc.

Therefore the most qualified firms in the use of poisonous gases were consulted with regard to the possibility of carrying out this treatment on a large scale. Since none of these firms had vacuum cells at their disposal, and also since after an accurate examination of the new library premises, it was established that it was impossible for technical reasons to use gaseous substances in the storerooms the fumigation was planned to be made in suitable premises and with a mixture of formaldehyde (which has a disinfecting action) and methyl bromide (which has a disinfesting action) for the books which revealed attacks of insects and microorganisms, and with formaldehyde only for those showing exclusively alterations of microbial agents.

Premises where treatments were carried out

For the fumigations with the mixture of the two above-mentioned gases, the firms entrusted with the treatment used an underground room of the same library.

The fumigations with formaldehyde alone were done by another firm which set up an installation of considerable dimensions (fig.1) in the underground rooms of the library in which it was possible to regulate during the course of treatments using the appropriate equipment (thermoventilators, humidifiers, thermostats, ventilators) the thermogravimetric values and favour the diffusion of the gas. In the two rooms described above that were used for treatments, metal book-cases were placed along the walls with open supports and punched shelves on which the books were placed in an open-fan-like position. Nevertheless since it is commonly known that formaldehyde has poor penetration power, the "Istituto di Patologia del Libro" carried out a series of tests to assess the effectiveness of the treatments.

Samples on which tests were made

The tests were made on pieces of paper and cloth taken from those books which showed serious microbial attacks, books which came from various rooms of the National Library of Rome.

In order to express an opinion, within the limits of the exhaustive possible, on the disinfecting action of the fumigants used, and in order to be able to estimate their diffusion in the rooms and

fig. 1



in the books, these samples were distributed in the interior and on the exterior of books in various established positions, keeping in mind the elements indicated below which in our opinion could have a determining influence on the results of treatments.

- a) Disposition of books in rooms
- b) Format of books and position of microorganisms on pages
- c) Residues of disinfectant on paper
- a) Disposition of books in rooms where treat-

ments were carried out

To establish whether a uniform diffusion of gas was obtained, during fumigations the samples were placed in the interior and on the exterior of the books in the various sectors of rooms destined for treatment.

- b) Format of books and position of microorganisms
- on the pages

In order to assess the penetration power of the disinfectants in the various parts of the books or in books of different formats, we placed fragments of each sample in 3 positions A, B, and C during treatment. Samples marked A were placed outside the books and were therefore freely exposed to the action of the gas, those marked B and C were placed inside the books, the former near the edge and the latter in the more internal part near the spine (dis 1).

The samples were placed in books of different format (4°, 8°, 16°).

Particularly complex was the problem of the disinfection of journals because the penetration of the gas was made difficult by both the format and the type of paper.

In order to assess the conditions under which the most effective disinfecting action was obtained, during some treatments samples were placed inside open volumes of journals at 180° (dis.2), both in correspondence with pages in between which little metal sticks had been placed to favour the penetration of the gas, and between pages

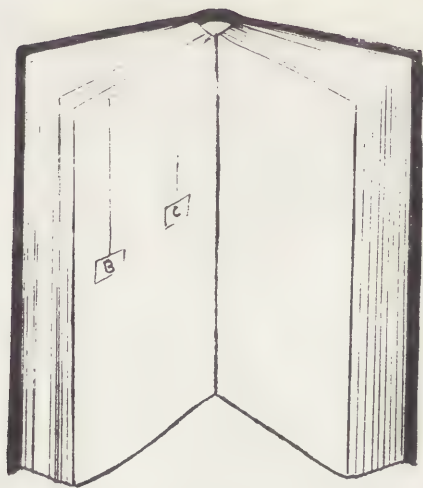


fig. 1



fig. 2

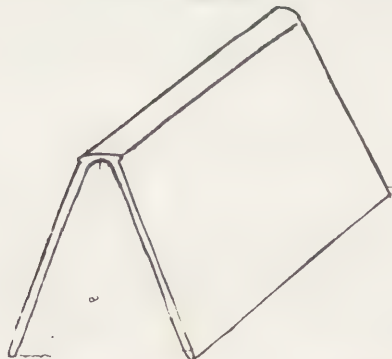


fig. 3

in close contact. However during the course of other treatments samples were placed both in the above-mentioned conditions (samples B and C), and inside books placed in a wigwam position (dis.3) (samples BV-CV).

c) Residues of disinfectants on the paper

In view of the fact that the elimination of formaldehyde from the treated materials is extremely slow, in fact several days are necessary to completely remove it, and considering the fact that the disinfectant residues could alter the results of the tests, we thought it advisable to place inside the books in each position 2 fragments of the same sample of which one was placed on the culture medium 4 days after treatment and one 15 days after treatment.

Treatments

The treatments to which the results refer were carried out with dosages of disinfectants and at the thermogravimetric values indicated in table 2. Formaldehyde was obtained through heating by trioxymethylene.

Testing methods

The treated samples which were kept in sterile surroundings after they had been extracted from the disinfecting chambers were placed 4 days and 15 days after the fumigations in Petri capsules at the bottom of which agar sabouraud had been placed and incubated at 30°C for 14 days.

Before the samples were placed on the agar they were washed in sterile distilled water. We used this device to eliminate eventual microbial spores, present in the air introduced into the disinfecting chamber after the fumigation, during degassing operations, spores which could have lodged on the samples and therefore altered the results of our research. Furthermore, in order to identify the microbial flora present on the samples of paper used for the tests and to assess the presence on these of bacterial and fungal spores likely to germinate, parallel to the treated series a "control" series was prepared, untreated with gaseous disinfectants.

The results were perceived after 7 days and 14 days of incubation.

Tab. 2

Treatments of book material of the National Library of
Rome with formaldehyde and methyl bromide

Treatments	Dosage formal- dehyde gr/m^3	Dosage methyl bromide gr/m^3	Temperature	Relative humidity	Duration of treatments	Position of samples	Percentage of samples on which treatment proved active	
							I Series	II Series
I Treatment	10 gr/m^3	-	30°C	70%	18 ore	A B C	8% 80% 8%	80% 80% 8%
II Treatment	10 gr/m^3	-	30°C	70%	23 ore	A B C	8% 8% 8%	85% 75% 80%
III Treatment	10 gr/m^3	-	30-33°C	86-94%	48 ore	A B C	95% 90% 95%	5% 80% 90%
IV Treatment	10 gr/m^3	-	31-33°C	85-95%	48 ore	A B C	100% 65% 70%	100% 75% 60%
V Treatment	10 gr/m^3	-	28-30°C	90-100%	48 ore	A B C BV CV	95% 85% 85% 95% 80%	95% 55% 55% 50% 75%
VI Treatment	10 gr/m^3	-	24-30°C	78-85%	46 ore	A BV CV	100% 100% 65%	95% 95% 85%
VII Treatment	10 gr/m^3	45 gr/m^3	18-28°C	58-64%	32 ore	A B C	87% 95% 75%	92% 55% 80%
VIII Treatment	10 gr/m^3	45 gr/m^3	25-27°C	62-68%	48 ore	A B C	75% 95% 65%	80% 92.5% 75%

Key: A Samples placed, during treatment, outside the volumes
B Samples " " inside (towards the external margin) of volumes
C Samples " " inside (towards the internal margin) of volumes
BV Samples placed, during treatment, inside (towards the external margin) of volumes in a wigan position
CV Samples placed, during treatment, inside (towards the internal margin) of volumes in a wigan position

Results

"Control" samples

In all tests we found on those untreated "control" samples a rich bacterial and fungal flora, flora on which the fumigants proved to be active in various dimensions.

Treated Samples

The results of tests carried out on hundreds of samples disinfected with formaldehyde alone or with the mixture formaldehyde-methyl bromide, are set out in table 2.

On examining the results of treatments I, II and III, it can be seen that there is no apparent difference between the percentage values concerning samples A, B and C placed during individual treatment outside and inside (towards the spine and towards the edge) of books of format 4-8-16, which demonstrates the considerable penetration of the fumigant between the pages of the books which were placed open in a fan-like position. On the contrary the comparison between the data concerning the 3 above-mentioned treatments clearly shows that by varying the parameters humidity-time of fumigant action, different results are obtained. In fact the percentage values of treatment III concerning samples on which the formaldehyde had acted for 48 hours with hygrometer values of 86-94%, were higher than those obtained in treatments I and II with times of 18 and 23 hours and relative humidity of 70%.

As for treatments IV, V and VI, during these treatments the samples as explained previously were put inside volumes of open journals at 180° (treatments IV and V) or placed in a wigwam position (treatments V and VI).

By comparing the percentage values concerning such fumigations, it is possible to ascertain that the penetration of the disinfectant towards the spine (sample C-CV) is difficult, however when the books are placed (open at 180° or wigwam-like), on the contrary on the more external part of the page towards the edge (samples B-BV) the results were more satisfying when the books were in a wigwam position.

fig. 2



Finally from a comparative examination of the data concerning treatments VII and VIII, obtained with the mixture formaldehyde, methyl bromide, some differences are shown.

In the course of treatment VII the destruction of the microbial flora was obtained on 87,5-95% of the samples placed outside the books, and inside them near the outer edge, and on 75-80% of the samples placed near the spine. The results concerning treatment VIII were on the other hand less satisfying than the former ones especially for the samples placed near the spine of the books. However the analysis of the percentage values obtained in this last treatment in individual sections of the room, in which as explained previously the samples were distributed, results which for reasons of briefness will not be referred to in this study, lead us to advance the hypothesis that the gases for reasons which have not been identified, were not diffused uniformly in the atmosphere, and penetrated the books with considerable difficulty.

TREATMENT OF THE BOOK MATERIAL OF THE ANGELICA LIBRARY IN ROME

Among the problems faced up to over the last few years in the field of vast scale treatment of book material, an interesting experiment in disinfection and disinfestation on the spot was the fumigation carried out in the Great Hall of the Angelica Library of Rome (fig. 2).

In 1972 in this large dimensioned Hall (length 27,70m, width 12m, height about 13m) damage caused by insects and microorganisms was discovered both in the wood shelves which covered nearly all the walls and in the books themselves. On these shelves which are of a considerable depth, about 100,000 paper volumes are arranged sometimes in double or triple rows.

To stop the destructive action caused by biological agents it was decided to do a fumigation with formaldehyde and methyl bromide. The Library Management entrusted the disinfecting and disinfesting work to a specialised firm and asked the Istituto di Patologia del Libro to carry out tests at the end of the work to see if during the course of treatment there was a good diffusion of the

75/15/7-16

gases inside the books, and consequently if the biological agents which had caused the damage had been destroyed.

The tests were carried out on samples of paper taken from the books from the same library which had sustained serious microbial injury.

In order to pass judgement within the limits of the possible, on the disinfecting action of the fumigants used, and to be able to estimate their diffusion in the locality and in the books which had been placed in a fan-like position, these samples were distributed on the outside and inside books of format 4°8°-16° in various positions near the edge and near the spine (following the methodology described in the previous paragraph b concerning the treatment at the National Library of Rome), and in books arranged in various parts of the Hall.

In fact, since it was thought that in such a room because of the large dimensions and depth of the book cases with their solid shelves, it would be difficult to obtain a uniform distribution of the gases, we thought it advisable to compare the results obtained on the right and left sides at 3 different heights (at about 1,5 and 8 meters from ground level). Consequently fragments of the same sample were placed in books arranged in various parts of the room. Furthermore in order to carry out a direct control of the disinfected book material, and to be able to better assess various results obtained on samples placed in books in the Hall at a height of about 8 meters, we also examined fragments of paper taken from volumes in this section after the fumigation.

Treatment

The treatment was carried out with a mixture of formaldehyde and methylbromide in the dosages and under the atmospheric conditions listed below:

Duration of treatment: 34 hours
Dosages: formaldehyde 10 gr. /m³ (obtained
for heating by trioxymethylene)
methyl bromide: 45 gr. /m³
Temperature: 20-25°C
Relative Humidity: 55-65%

Testing methods

The same methods that were used for the tests carried

out on book material from the National Library of Rome and described in the previous paragraph "testing methods".

Results

Sample control

On all the untreated "control" samples the presence of numerous schizomycetes and mycetes was found.

Treated Samples (table 3)

The tests carried out on samples treated with the above-mentioned dosages of formaldehyde and methyl bromide and distributed at various heights in the Hall and in books of different format, have clearly shown that the diffusion of the fumigants was not uniform in all sectors of the room. From the examination of table 3 it can be seen that at a height of about 1 meter from the floor the gases were active on about 70% of the samples placed during treatment both in the exterior and interior of the books (near the edge and near the spine).

More satisfying results were obtained at a height of about 5 meters from the floor where the formaldehyde and methyl bromide had destroyed the bacterial and fungal forms on about 1'80% of the pieces of paper which during treatment were in the most external part of the book near the edge, and on 84% of those placed near the spine.

At a height of about 8 meters positive results were obtained on 71% of the samples placed in the most external part of the books near the edge, while the destruction of the microorganisms was achieved on only 25% of the samples placed near the spine.

The data concerning this last group led us to carry out a further examination of pieces of paper removed after disinfection from the internal part (near the spine) of 40 books submitted to the treatment with formaldehyde and methyl bromide, and arranged on the shelves in this section of the Hall. The controls carried out enabled us to assess the absence of active forms on more than 90% of these fragments.

Percentage of samples of the hall of the Angelica Library of Rome on which formaldehyde and methyl bromide proved active

Position of samples	I Control	II Control
A	71%	71%
B	71%	71%
C	71%	66%
B.I.	84%	79%
C.I.	87%	84%
B.II.	84%	71%
C.II	25%	25%
CV	92,5%	90%

Key: I Control carried out after 7 days of incubation
 II " " " " " 14 " " "

A Samples placed, during treatment, outside the books at distance of about 1 meter from ground level

B Samples placed, during treatment, inside (towards the external margin) of books placed on shelves at a distance of about 1 meter from ground level

C Samples placed, during treatment, inside (towards the internal margin) of books placed on shelves at a distance of about 1 meter from ground level

BI-EI Samples placed, during treatment, in the same position as the former ones inside of books placed on shelves at a distance of about 5 meters from ground level

BII-CII Samples placed, during treatment, in the same positions as the former ones inside of books placed on shelves at a distance of about 8 meters from ground level

CV Samples taken from books that during treatment were placed on shelves at a height of about 8 meters. These samples were taken from the internal part of the volumes

CONSIDERATIONS OF RESULTS

The results concerning treatments carried out with ethylene oxide in vacuum chambers, and with formaldehyde and methyl bromide in the Hall of the Angelica Library of Rome and in rooms of the National Library of Rome, suitably equipped for the treatment of books lead us to make the following considerations:

a) Ethylene oxide if used in determined dosages and conditions permits the total destruction of the microorganisms in all parts of the books even if the vacuum is not made before the introduction of the gas.

b) With formaldehyde and methyl bromide in particular cases it is possible to disinfect and disinfest storerooms with wooden shelving containing many ten thousands of books in 24-48 hours. However, since formaldehyde especially has a weak power of penetration, it is necessary to leave the books open in a fan-like position to facilitate the penetration of the gases. Even using this device the total destruction of the microorganisms is not obtained, above all in the most internal parts of the books near the spine.

Finally it is advisable to point out that formaldehyde if used repeatedly provokes oxidation processes on the metal shelving, a phenomenon which occurred in the premises of the National Library which were equipped for the disinfection of book material.

c) As for the Hall of the Angelica Library, where the treatment with formaldehyde and methyl bromide was chosen, after the need to destroy the biological agents which had damaged both the books and the shelving had been established, here the results were less satisfying than those obtained at the National Library. However, in our opinion this is due to the fact that fumigations in large rooms with high ceilings always present considerable difficulty, even if all necessary devices are used to obtain a uniform diffusion of the gases (rational positioning of book material, ventilators etc.), and to obtain those atmospheric conditions which are indispensable for an effective action on biological agents (regulation of temperature and relative humidity).

d) The regulation of temperature and relative humidity during fumigations whether carried out

75/15/7-20

in suitable chambers or in book storerooms, is essential for the destruction of the microbial flora. However, in order to obtain the best thermogravimetric values inside the books, it is necessary to place the books in the climatic conditions, chosen for the treatments, at least 24-48 hours before the introduction of the gas.

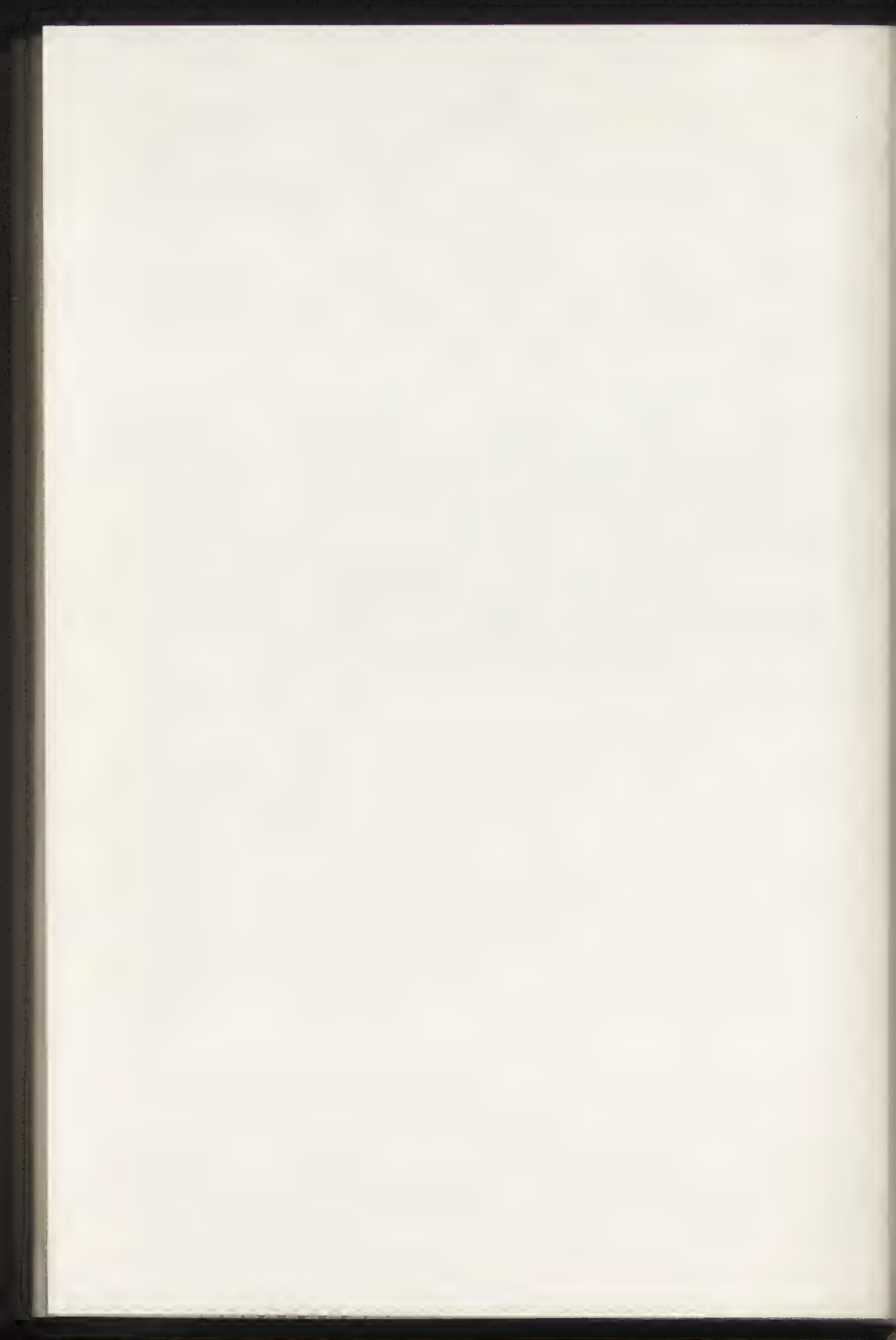
The results obtained clearly show on the one hand the possibility of carrying out disinfections and disinfestations on a wide scale in libraries using formaldehyde and methyl bromide, and on the other hand also show the expediency of giving preference whenever possible to ethylene oxide which has a high penetration power, rather than the two above-mentioned gases. This fumigant until now has been used for the treatment of books, always in an autoclave, but it cannot be excluded that on the basis of the experiments carried out by us with dosages of 250 gr./m³ it could also be used with the necessary precautions in rooms.

SUMMARY

In Italy over the last few years numerous experiments in the field of disinfection and disinfestation of books have been carried out with ethylene oxide, formaldehyde and methyl bromide.

Ethylene oxide was used for the treatment of books damaged by floods belonging to the National Library of Florence. Recently in the chamber of the "Istituto di Patologia del Libro" many tests were carried out with this gas which permitted us to estimate its penetration power inside the books, and the determining influence exerted, with the same dosages by the disinfecting action time.

Furthermore, treatments of ten thousands of books with formaldehyde and methyl bromide were carried out at the new National Library and the Angelica Library in Rome. An experimentation was carried out to assess the diffusion of the fumigants in the ambients and in the books. The results obtained have clearly shown the possibilities and limitations of the application of formaldehyde and methyl bromide in book storerooms.



THERMAL ANALYSIS STUDY OF THE DETERIORATION OF
ETHNOGRAPHIC CARIBOU SINEW AND SUGGESTED TREATMENT

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INTRODUCTION

In the fabrication of ethnological artifacts tendon sinew has been widely used as thread, also for affixing decorative beadwork onto wool and leather fabrics and for fastening elements of wood boxes. Although collagen, the main component of sinew, is a very durable material in many cases it deteriorates over the years to such an extent that the stitches break resulting in the separation of the fitted parts.

The mechanism of the ageing process of sinew is not known and little guidance can be given concerning the restoration, preservation or even optimum storage conditions of artifacts containing sinew components. The study of the environmental factors affecting the durability of sinew, notably ultraviolet radiation and cyclical temperature and relative humidity changes appears to be desirable.

It may be noted that although only sinew samples were included in the experiments, the results are of relevance to leather and parchment. In contrast to leather, where the individual collagen fibers are woven together in a network and embedded in the ground substance of the connective tissue, in tendon, the collagen is in the form of bundles, which are arranged in a parallel fashion and are surrounded by some form of outer covering. Tendon, therefore, can be considered as a special form of leather in which the physical properties of the tissue are determined by the individual fiber bundles.(1)

EXPERIMENTAL

The material was caribou sinew acquired from Canadian Natives. The one to four year old bundles (approximately 60 cm. long) were sufficiently flexible that they could be separated into simple fibers in the dry state.

The length changes of the specimens during heating were measured with the aid of a DuPont Model 990 Thermal Analysis System in conjunction with a Model 942 Thermomechanical Analyser (TMA), which utilizes a movable core, linear, variable differential transformer. The sensitivity in all runs was 50 mils/inch of chart (0.05 cm/cm chart) and the loading was 1 g. Heating was controlled at 5°C/min rate between 25 and 320°C. Positive and convenient clamping of the fiber sample was achieved by means of two cleaved aluminum spheres crimped at the ends. The length of the prepared specimen was 0.5 inches (1.27 cm).

The Differential Scanning Calorimeter (DSC) cell of the same system was used for the determination of the enthalpy changes in the temperature range of 25 to 300°C.

In order to prevent reaction with atmospheric oxygen at elevated temperatures the sample was hermetically sealed in a metal container. The heating rate was 5°C/min. An empty sealed cup served as reference.

An Instron Testing Machine was used to determine the ultimate tensile strength, the stress at the breaking point of the sinew fibers. A crosshead speed of 2 cm/min was employed with a load cell of 100 kg maximum capacity.

The x-ray diffraction photographs were obtained in a Debye-Scherrer type camera (Philips PW 1024) using copper K α irradiation with Ni filter and operated at 40 KVolts and 25 mAmps. The pliability of the fibers was tested in a fold endurance testing machine. The Tinius Olsen Number 1 Model which is suitable for materials of low elongation characteristics was used. The number of folds endured was determined under a slight constant tension, derived from 0.4 kg load.

The samples were aged in an Atlas Weather-O-Meter equipped with a 6000 Watt water cooled Xenon arc lamp and filters, which produce spectral distribution and intensities of the irradiating light similar to that of natural daylight. The fluorescence emission peak of the lamp is at 340 nm. In addition the temperature and relative humidities can be controlled. The radiative intensity was selected to be 46 W/cm², while the temperature was controlled at 55°C and the relative humidity at 50%. One complete cycle consisted of irradiation for two hours followed by cold water (12°C) spraying in darkness for 40 minutes. The

in each 24 hour period the samples were exposed to 18 hours of irradiation and 6 hours of spraying. Initially, in the first three weeks samples were removed from the Weather-O-Meter every 72 hours for testing, but at later stages only once a week. The specimens obtained were subjected to DSC and TMA to detect changes due to ageing.

RESULTS AND DISCUSSION

1. Length Changes of the Native Fiber

A typical TMA curve for an unaged native fiber is shown in Fig. 1. At first the fiber contracts in an almost linear fashion until approximately 180°C , at which temperature a large contraction commences. On further heating the fiber expands above 212°C , but at higher temperatures a second contraction occurs. At approximately 230°C a very large expansion is always obtained.

These features are attributed to the following physical changes: glass transition, followed by crystallization and finally melting of the collagen to yielding a viscous, denatured substance.

Collagen fiber is an anisotropic material in which amorphous regions are interspersed with crystalline ones. (1) The amorphous substance is the more reactive and on heating it is affected first. At higher temperature the non-crystalline phase suffers further disorientation and the fiber contracts. This behaviour is characteristic of most polymers; polyethyleneterephthalate and Nylon 66 fiber can be cited as examples. (2)

The glassy state is invariably associated with the existence of strong molecular interactions: H-bond and van der Waals forces, and is a thermodynamically metastable state. The first derivatives with respect to temperature and pressure of the free energy, entropy and volume respectively, do not change discontinuously during transition but the second derivatives: expansivity, compressibility, heat capacity change abruptly at the glass transition temperature (3, 4, 5, 6). For the detection of the glass transition dilatometry is frequently utilized. The initial section of the length change curve of Fig. 1 indicating a sudden change of the coefficient of expansion at approximately 200°C , would be consistent with a glass transition occurring at this temperature and is assumed to have taken place. This aspect will be further discussed after introducing the DSC and X-ray results.

2. Thermal Changes of the Native Fiber

The differential thermograms of a native fiber as obtained with the DSC in two sensitivities are shown in Fig. 2. The large endothermic peak at 123°C is undoubtedly due to loss of water. The small endothermic peak is caused by melting of the crystalline component of the glass transition process. Usually the amorphous substance contains a small amount of crystals which melt over a range of temperature (7). The small exothermic peak following the glass transition would need more study to be sure of its real existence. If it does exist it could be accounted for on the basis of some crystal growth occurring. On further heating the collagen turns into a brown viscous mass, a process accompanied with endothermic heat change and large expansion. This transition can be called melting and total denaturation consisting of the destruction of the rigid helical structure of collagen into a randomly coiled gelatin.

3. X-ray Diffraction

Further X-ray diffraction studies are underway to confirm the interpretation of the DSC and TMA curves and the following conclusions should at this time be considered to be tentative. Fresh sinew at 25°C has the expected axial oriented linear structure. On heating to 200°C, the glass transition temperature, there is a partial melting of crystals followed by a slight crystallization on further heating. After heating to about 250°C the molten mass is of course amorphous. XRD lines are very weak, making any interpretation difficult.

4. Tensile Strength and Folding Endurance

The tensile strength of the native sinew was found to be approximately 20 Kg/mm², which is similar to the values compiled by Viidik (9) & Elliot (11). The tensile strength varies, and of course, greatly with the species and the type of tendon. Although it is an inherent property of the material, test results depend on various parameters, i.e. shape, size and moisture content of the specimen and speed of crosshead travel of the testing machine. (12) An attempt was made to select only those specimens, the diameter of which did not vary more than 0.001" (0.0254 mm) from 0.009" (0.2286 mm). The most serious difficulties were caused by the uncertainties in the cross sectional area determination, giving rise to discrepancies in the results. As shown in Table 1 samples exposed in the Weather-O-Meter for only four days suffer significant loss of strength: from 20 to 10 kg/mm². The deterioration of the mechanical properties was observable also in the

dramatic diminution of the folding endurance: while the native fiber could be flexed 23,652 times, exposure for 4 days to the conditions of the environmental chamber reduces (Table 2) to 65.

5. Effect of Ageing

The temperature values of the anomalies are shown in Fig. 3. After 72 hours of irradiation the value of T_g increases significantly from 198°C to 205°C , but on further exposure it changes only very slightly, if any. Within the experimental error the T_c , T_m and T_b versus irradiation time graphs are essentially horizontal. The lines drawn in Fig. 3 have been fitted by the method of least squares.

It is generally accepted (10, 13, 14, 15) that ageing in connective tissue is due to the increased amount of intra and intermolecular crosslinks, resulting in increased structural crystallinity and decreased elasticity. The mechanism of ageing in vitro is similar to that taking place in vivo. It has been shown that tendon fibers originating from young animals undergo ageing during storage presumably caused by alterations in the spatial arrangement of the collagen helix. (15) The increase in T_g as found in the first 72 hours of irradiation is to be expected according to this explanation because the glass transition temperature rises with increased inter-chain interactions as shown by Krause et al (4). This effect is especially pronounced when the electrostatic interactions are large. T_g was found to decrease when solvent caused swelling of the solid. (5) Ultraviolet radiation is known to induce additional crosslinking reactions in natural macromolecules (16).

6. Evaluation of Sinew from an Artifact

At this point the answers were sought to the following questions:

- (a) Are the characteristics of the naturally aged sinew artifacts similar to those of the Weather-O-Meter exposed specimen?
- (b) What practical measures are effective in restoring or at least preserving aged sinew artifacts?

Experimental work in these areas is, however, greatly hindered by the destructive nature of the thermoanalytical and mechanical tests. The Ethnology Division of the National Museums of Canada could not permit the taking of samples large enough for the analyses directly from ethno-

logical artifacts. In order to make a gross evaluation of a naturally aged sinew, permission was obtained to remove a loose piece, 2 cm long, for testing. The artifact from which the piece of sinew came was a beaded tobacco bag (Cat.No.II-D53)(Fig.4), which originated in the late 19th century and was collected in 1928. Sinew had been used for stringing the beads and appears to be generally in fair condition except in the border areas, where it broke causing the loss of some beads. The sample size was sufficient only for TMA analysis. The transition temperatures were found to be approximately the same as in the native fiber. The glass transition was at 193°C , crystallization at 207°C and melting at 237°C . The sample broke at 247°C . These values are very similar to the corresponding temperatures for the unaged specimen, suggesting that the cause of the deterioration was other than the processes occurring in the Weather-O-Meter.

As the mechanical properties (brittleness, strength, etc.) of the artifacts are impaired - although not uniformly throughout the whole sample - deterioration has obviously occurred. I have assumed this deterioration to be the result of abrasion and desiccation. Had there been sufficient quantity of this sample available these predictions could have been confirmed by the determination of the water content or by DSC showing a reduced water loss on heating.

Attempts to Restore Artificially Aged Sinew

Attempts were made to improve the mechanical strength of naturally aged fibers which for lack of other means we could only prepare by ageing fresh fibers in a Weather-O-Meter. A specimen was irradiated with a total exposure of 190 Watt/cm^2 at 55°C and 50% R.H. The aged fiber was impregnated by submersion in a 25% glycerine solution in ethanol for 24 hours at room temperature. It was left to dry out in the air for 48 hours. Although the fiber appeared to be supple and pliable in comparison with the untreated, its tensile strength was found to be less (3.13 Kg/mm^2) than the untreated but similarly aged companion specimen (8.73 Kg/mm^2). It became glassy in appearance which others have indicated may be the result of complete penetration of highly hygroscopic liquid and subsequent separation of the individual fibrils.

The experiment with glycerine treatment clearly indicated that better results may be expected with incompletely penetrating liquids. In this way the rigidity of the fiber can be eliminated without the inner core of the fiber losing its strength. This scheme resembles to a

degree the situation in vivo (11) i.e. the sinew is covered with a sheath, which in many instances take care of lubricating its surfaces with a synovial-like fluid, without loosening up its structure by complete penetration.

For a partially penetrating liquid, Polyethyleneglycol 1500 (Carbowax 1500) in isopropylalcohol was selected. The concentration was 27% and the solution also contained 5% glycerine. The fiber, aged for four days, was kept submerged in this solution for 27 hours. The tensile strength of the treated sample was 17.9 Kg/mm^2 , compared to that of the untreated sample, which was found to be 18.2 Kg/mm^2 . Thus the treatment did not affect the tensile strength. However, the stiffness was greatly reduced.

In another experiment, Neutralfat SSS (a stabilized olein soap) made by Schill and Seilacher Co., Boeblingen, Wuerttemberg, German Federal Republic, was also applied as an impregnating liquid (50% alcohol solution). The tensile strength of the specimen did not suffer any reduction due to treatment (20.0 Kg/mm^2 after and 18.2 Kg/mm^2 before the treatment). This is in contrast to the effect of an aqueous solution of formaldehyde and sulphited sperm oil (Lipoderm Liquor 2 made by BASF) in which case the tensile strength of the unaged fiber was sharply reduced from 24.7 Kg to 12.43 Kg and 12.10 Kg/mm^2 in glycerine and at the same time the stiffness increased. Experiments with various treatments are continuing.

CONCLUSIONS

Exposure to UV radiation combined with high humidities and temperature and liquid water induced changes in the thermomechanical properties of collagen. This effect appears to be similar to those observed in collagen with increasing age. They may be either due to increased cross linking, or decreased intramolecularly bound water or a combination of both. (17) The result of either of these mechanisms is an increased stiffness. Other factors such as desiccation, abrasion, SO_2 , etc. may be at least as important in museum objects.

As the ageing processes are usually considered to be irreversible, the most promising avenue open for minimizing the danger of breakage is to increase the pliability. It was found that this can be achieved with treatment by suitable lubricating agents.

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Acknowledgements

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ABSTRACT

Caribou sinew specimens were exposed to UV radiation, combined with increased temperature and humidity in a Weather-O-Meter. The changes of the thermomechanical parameters were monitored as a function of the absorbed radiation. The anomalies of TMS and DSC curves could be interpreted in terms of phase changes. The result of preliminary x-ray diffraction studies were consistent with this interpretation. Ageing was found to increase the glass transition temperature and to decrease the melting point. Similarly tensile strength and pliability decreased with ageing. Treatment aiming to increase the pliability appears to be the only method to improve the mechanical properties. Alcoholic solution of polyethyleneglycol or stabilized olein soap were found suitable for this purpose.

Hours Exposure in Weather-O-Meter	0	72	126	180	324	378	1152
Radiation Exposure in Watt/cm ²	0	11.9	20.9	29.8	53.7	62.6	191
load at breaking in g	1348 670 1800 1070 1458 1830 1085 1060 1290	495 530 718 850	720 310 510 740	735 150	639 330 450	570 810 310	278 298 215 701 710
Average g		648	575	442	473	563	563
Average Ultimate tensile strength Kg/mm ²	20	10	8.91	6.85	7.33	8.73	8.73

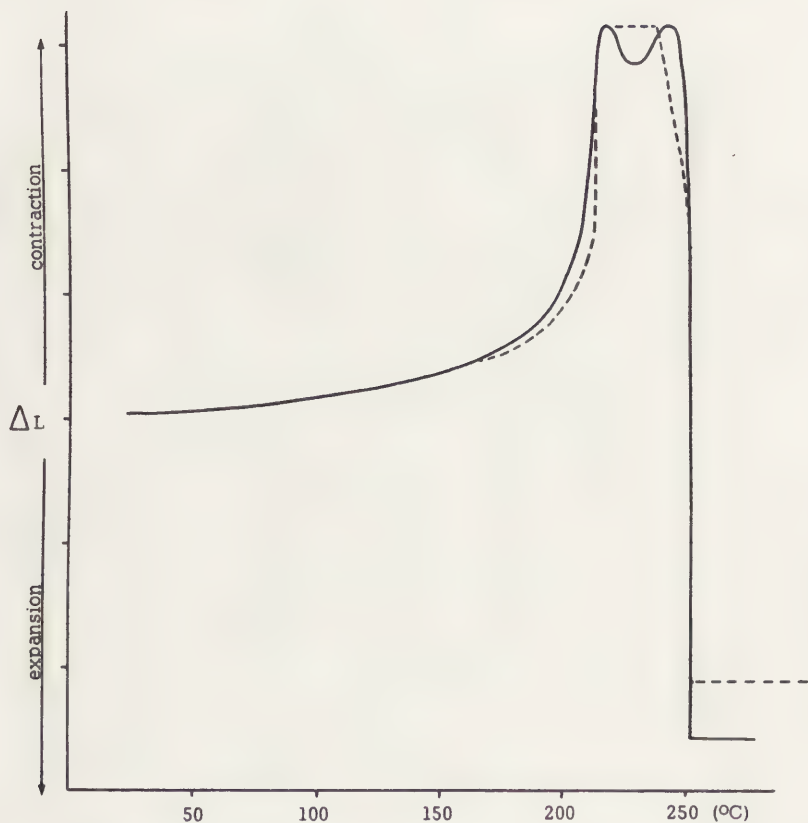
Tensile strength of sine wave specimen as a function of Weather-O-Meter ageing. Conditions of test described in text

TABLE I

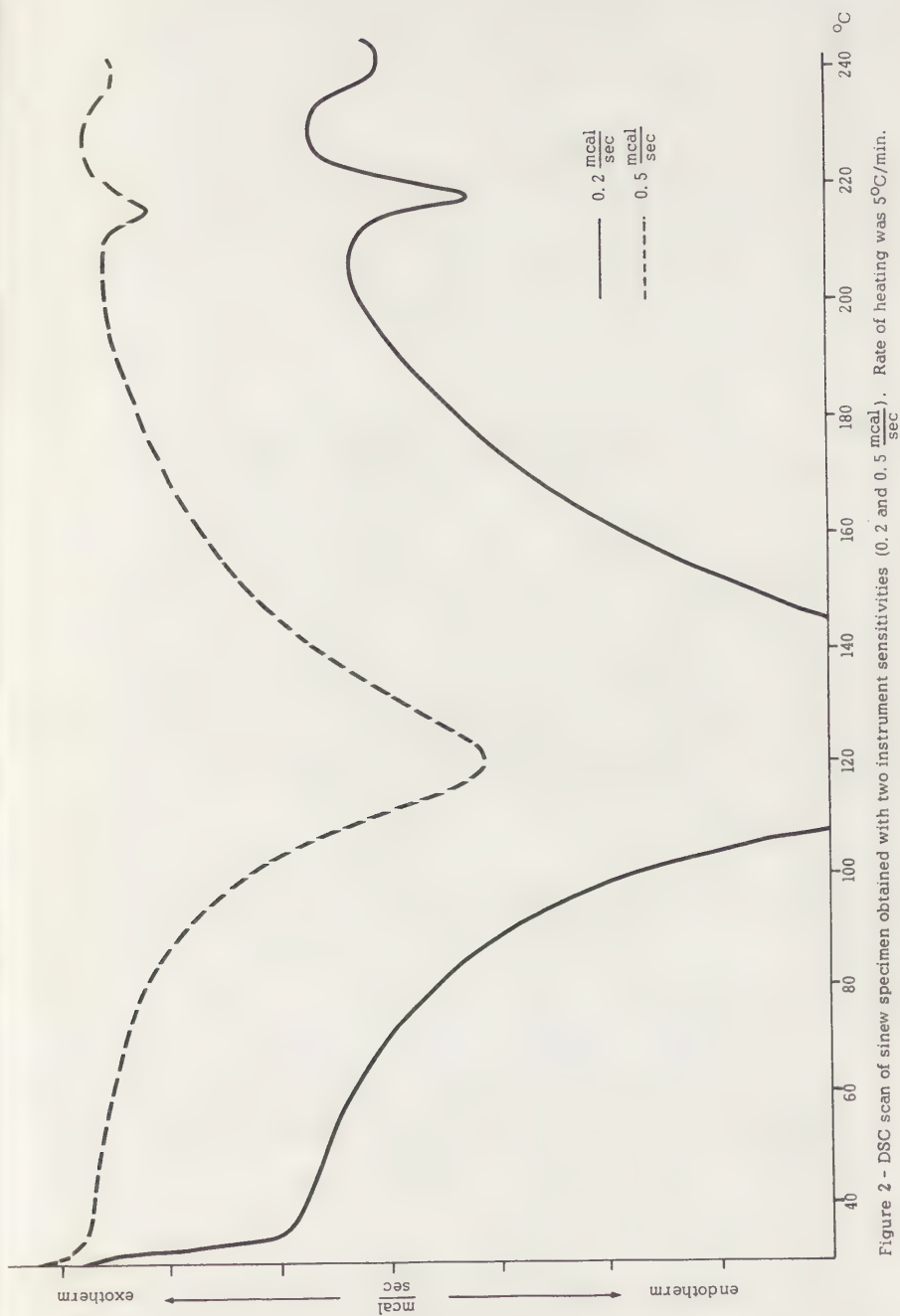
Hours Exposure in Weather-O-Meter	0	72
UV radiation exposure watt/cm ²	0	11.9
Treatment	none	Neutralfat SSS
No. of flexes	7456 47252 3984 4332 3461 83221 59587 3576 60051	27539 22541 3397 13636 4191 6126 2598 17496 71532
Average of flexes	23652	18748
		65
		363 25 1 0.5 0.5 0.5

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Table 2. Folding endurance of sinew fiber as a function of chemical treatment and artificial aging.



TMA scan of unaged (—) and 810 hrs aged (---) sinew. (134.136 Watt/cm² total irradiation.) Rate of heating was 5°C/min.
Fig. 1



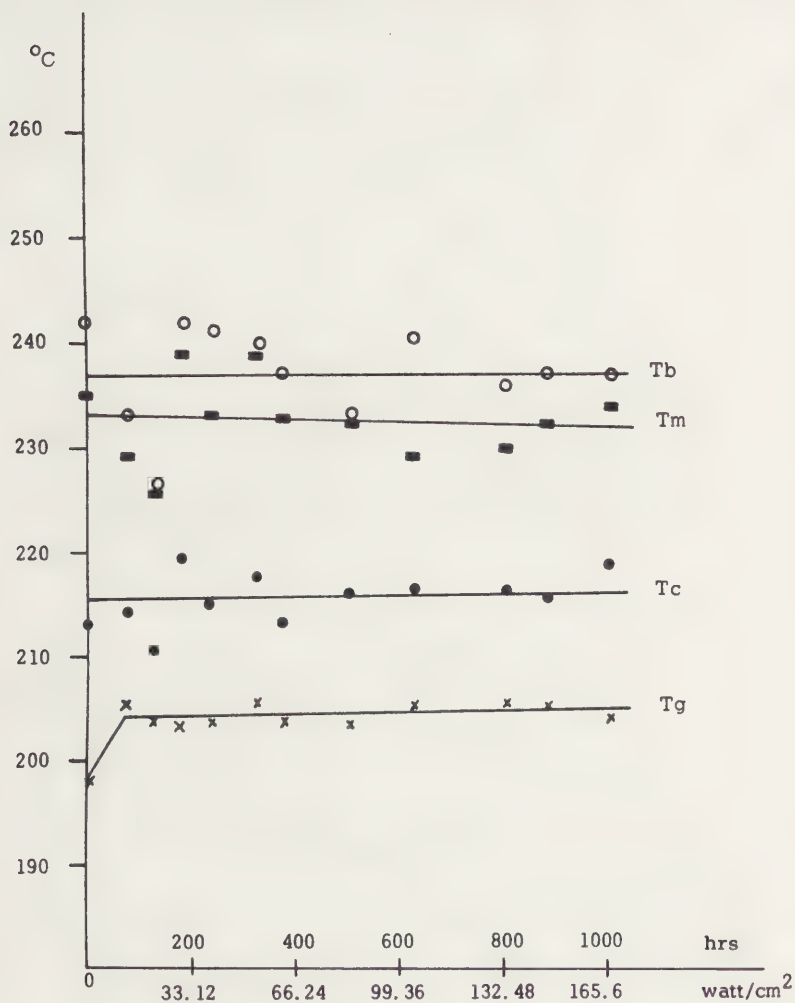


Fig. 3 Temperature of glass transition (T_g), crystallization (T_c), melting (T_m), breaking (T_b) of sinew as a function of absorbed energy or time of irradiation.



Fig. 4 Beaded tobacco bag artifact (Cat. No. II-D 53)



ÉTAT DES TRAVAUX EFFECTUÉS SUR L'ANALYSE DES CONSTITUANTS
DES ENCRE NOIRES MANUSCRITES PAR DEUX TECHNIQUES:
CHROMATOGRAPHIE SUR COUCHE MINCE ET ÉLECTROPHORÈSE

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RESUME

Ce rapport se propose de résumer l'état actuel des travaux réalisés dans l'identification des composants supposés avoir été utilisés dans la fabrication des encres noires manuscrites antérieures au XVIIe siècle.

Dans une première étape, nous avons étudié les substances naturelles entrant dans la composition de ces encres, à savoir : les liants glucidiques, les liants protéiniques, les substances tannantes. Les techniques utilisées sont la chromatographie sur couche mince uni et bidimensionnelle et l'électrophorèse haute tension.

La chromatographie sur couche mince bidimensionnelle appliquée à deux substances particulières : la gomme arabique (liant glucidique) et la noix de galle d'Europe (substance tannante), améliore les résultats obtenus pour ces mêmes produits en chromatographie sur couche mince unidimensionnelle.

L'électrophorèse donne de bons résultats en ce qui concerne les acides aminés et semble prometteuse pour résoudre le problème de la séparation des acides uroniques contenus dans les liants glucidiques.

De l'ensemble des expériences réalisées, il résulte que l'identification des liants dans les encres noires médiévales est relativement aisée, alors que celle des substances tannantes pose encore des problèmes.

Cet article fait suite à une précédente communication au Congrès de l'I.C.O.M. en 1972 (1), particulièrement axée sur l'histoire des encres noires manuscrites et leurs perspectives d'analyse. Cette étude littéraire préalable montre que les encres noires (tout au moins les encres noires médiévales) ont une composition assez caractéristique d'une aire géographique ou culturelle donnée : très schématiquement, rappelons que la répartition s'effectue ainsi :

Occident - Encres ferro-tanniques : à une macération ou décoction de substances tannantes on ajoute un sel de fer ou de cuivre (en général un sulfate). Le précipité noir obtenu est maintenu en suspension par l'adjonction d'un liant glucidique (presque toujours de la gomme arabique).

Extrême-Orient - Encres au carbone (fondamentalement différentes des précédentes) : il s'agit de bois calcinés ou de noir de fumée mélangés à un liant protéinique. La présence de parfums (clous de girofle, musc, camphre) est souvent mentionnée dans les recettes. On relève également dans les textes, qu'en plus de ces ingrédients de base, on ajoute parfois une solution de produits végétaux.

Afrique du Nord et Moyen-Orient - Encres mixtes

- Type A - encre au carbone avec adjonction d'un sel de fer (sulfate)
- Type B - encre au carbone avec adjonction de substances tannantes en décoction ou macération.

Ceci étant posé, signalons que ce rapport se propose de résumer l'état actuel des expériences réalisées dans l'identification des composants des encres noires manuscrites*. Ne seront mentionnés que les essais qui ont donné des résultats positifs en excluant ceux (et ils sont nombreux surtout en ce qui concerne le choix des éluants utilisés en C.C.M., des tampons en électrophorèse, des révélateurs, etc ...) qui ont été réalisés sans donner de résultats probants.

* Il s'agit plus particulièrement des constituants supposés avoir été utilisés dans la fabrication des encres, antérieurement au XVIIe siècle.

LES SUBSTANCES NATURELLES

Dans une première étape, il était nécessaire de mettre au point les différentes techniques d'analyse des substances naturelles entrant dans la composition des encres.

Les substances naturelles sont de trois sortes : liants glucidiques ; liants protéiniques ; substances tannantes.

Les analyses s'effectuent en premier lieu sur "macroquantité" de 10 milligrammes environ, puis vérifiées sur "microquantité" de 0,3 milligramme, les prélèvements prévus sur manuscrits ne devant jamais dépasser ce dernier ordre de grandeur.

En ce qui concerne les liants, leur étude m'a été simplifiée par les expériences réalisées dans ce domaine par de nombreux chercheurs et en particulier Mme FLIEDER*, Mme MASSCHELEIN**, Melle ROELOFS***.

Les deux techniques que nous avons utilisées sont : la chromatographie sur couche mince et l'électrophorèse. Nous n'entrerons pas dans les détails opératoires de la C.C.M. largement pratiquée dans ce genre d'analyse, préférant nous étendre plutôt sur ceux de l'électrophorèse (voir annexe).

LES LIANTS GLUCIDIQUES

C'est surtout de gomme arabique dont il est question dans les recettes d'encres, mais comme certains textes font mention parfois de "gommes d'arbres" sans plus de précision, il était nécessaire de pouvoir différencier certaines d'entre elles (gomme arabique, gomme de cerisier, gomme adragante, par exemple).

L'hydrolyse (2) de l'échantillon s'effectue en milieu acide (HCl 3 %) dans une ampoule scellée pendant deux heures à 105°C****. Le volume d'HCl est de 0,5 ml pour les prises d'essai "macro" et de 0,2 ml pour les prises d'essai "micro".

Chromatographie unidimensionnelle sur couche mince : la chromatographie de l'hydrolysate s'effectue sur chromatoplaques de gel de silice prêtes à l'emploi (Merck). Quelques variantes sont à signaler selon que l'adsorbant est étalé sur support d'aluminium ou support de verre.

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**** Mme FLIEDER annonçait (2) que 24 heures d'hydrolyse pour les sucres semblaient un temps trop long, effectivement, deux heures se sont avérées suffisantes.

- Dans le cas du support d'aluminium, on peut chromatographier directement l'hydrolysate acide sans le neutraliser (afin d'éviter les risques de perte sur microquantités) en prenant soin de tamponner la chromatoplaque par trempage dans un tampon phosphate à pH 8* (pour 100 ml de solution tampon : 96,5 ml de Na_2PO_4 M/15 + 3,5 ml de KH_2PO_4 M/15). La chromatoplaque une fois bien imprégnée de tampon est séchée à l'étuve et activée quelques minutes à 105°C avant le dépôt de l'hydrolysate.

- Pour une chromatoplaque de gel de silice sur support de verre, une neutralisation de l'hydrolysate s'impose** sur résine échangeuse d'ions (Amberlite IRA 68) (5). La résine est préalablement lavée puis maintenue en suspension dans de l'eau distillée. On ajoute alors grain à grain dans l'ampoule contenant l'hydrolysate la quantité de résine nécessaire à la neutralisation. Pour éviter toute perte de produit, on prélève directement dans l'ampoule l'hydrolysate neutralisé à l'aide d'une micropipette et on dépose sur la chromatoplaque préalablement activée à 105°C quelques minutes à l'étuve.

L'élution s'effectue avec le mélange suivant (4) :
isobutanol, acide acétique, eau - 5 / 4 / 1

Cet éluant était utilisé au C.R.C.D.G. pour l'étude des liants glucidiques des couches picturales des enluminures. Après en avoir essayé une dizaine d'autres, nous avons retenu celui-ci qui permet une des meilleures séparations des sucres en C.C.M. unidimensionnelle.

La révélation s'effectue par pulvérisation du révélateur sur la chromatoplaque, puis celle-ci est passée à l'étuve à 105°C quelques minutes. Deux révélateurs donnent de bons résultats :

- 1 ml d'acide orthophosphorique + 9 ml H_2SO_4 + 20 mg naphtorésorcinol (4-6-7).

Les sucres apparaissent sous forme de spots bleu ou violet sur fond rose.

- à une partie d'orcinol 1,6 % aqueux, on ajoute 6 parties d' H_2SO_4 1 N*** (8-9).

Les sucres sont de toutes les couleurs sur fond jaune.

* Cette technique dérive de la méthode de Lombart (3) qui préparait son adsorbant avec un tampon pH 8.

** En effet, la plaque de gel de silice sur verre résiste très mal à un trempage dans le tampon phosphate pH 8.

*** Ce procédé mis au point pour une étude quantitative des glucides en solution nécessitait de l'acide sulfurique à 60 %. Nous l'avons remanié pour permettre la pulvérisation du réactif sur la chromatoplaque sans dégradation du support en vue d'une étude qualitative des sucres.

Remarques : 1) la lecture des chromatoplaques du support de verre est facilitée par la possibilité de déceler par transparence l'existence de certains spots.

2) Signalons que le révélateur à l'orcinol permet une détection d'un plus grand nombre de spots (certains d'entre eux d'ailleurs n'ont pas encore pu être identifiés).

Des trois gommés étudiées, la gomme arabique contient du rhamnose en plus grande quantité, ce qui nous permet lorsque nous travaillons sur des "microquantités" de mieux la différencier des autres.

La présence de xylose ou de rucose (de Rf très voisins donc difficiles à différencier) exclut la gomme arabique. Les acides uroniques (galacturonique pour la gomme adragante et glucuronique pour la gomme arabique et celle du cerisier) migrent peu et leur Rf très proche permet difficilement, surtout en microquantités, de trancher sur la présence de l'un plutôt que de l'autre. Nous avons pensé pouvoir améliorer nos résultats en pratiquant une C.C.M. bidimensionnelle ou en utilisant l'électrophorèse.

Chromatographie bidimensionnelle sur couche mince : elle a été réalisée pour le moment dans le cas de l'hydrolysat de gomme arabique. Nous avons utilisé le gel de silice sur support d'aluminium dans les conditions opératoires signalées précédemment (tamponnage à pH 8, séchage, activation) ; et le naphtorésorcinol comme révélateur.

Les meilleurs résultats ont été obtenus en utilisant le couplage suivant :

Eluant (A) : chloroforme/alcool méthylique/eau/acide acétique
65 / 25 / 0,4 / 0,1 (10)

Eluant (B) : eau / propanol / acide acétique 30 / 60 / 10*

Une remarque s'impose avant de poursuivre : il semble que, de tous les éluants essayés, l'éluant (B) soit celui qui donne une meilleure migration des acides uroniques.

Nous avons essayé de permuter ces éluants :

éluant A $\xrightarrow{\uparrow}$ éluant B puis éluant B $\xrightarrow{\uparrow}$ éluant A

Dans les deux cas, les résultats sont bons. Le nombre de spots décelés (bien que non encore tous identifiés) est supérieur à celui d'une C.C.M. unidimensionnelle.

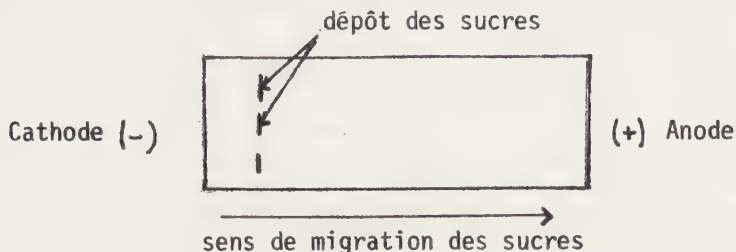
S'il n'est pas nécessaire d'utiliser cette technique systématiquement, ce procédé semble pouvoir être retenu pour des cas particuliers lorsque la résolution en unidimensionnelle pose un problème.

* Communication orale de Mme L. SZABADOS . Institut de Chimie des Substances Naturelles à Gif-sur-Yvette . France.

Electrophorèse : des quelques essais réalisés sur les glucides, il ressort que les sucres se comportent comme des anions en tampon borate pH 9

(H_3BO_3 0,62 g. + $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ 7,63 g pour 1 litre solution tampon).

Le dépôt des sucres a lieu dans ce cas (voir annexe) le plus près possible de la cathode. De ce fait, la migration peut être plus longue et la séparation meilleure.



Conditions opératoires : voltage 4000 volts, temps : 40 minutes.

Deux papiers ont été utilisés : Schleierg Schnell 2040 B et
Schleierg Schnell 2043 a

Deux révélateurs sont à retenir :

- 1) 1,47 g. d'acide ortho-phosphorique sont dissous dans 100 ml d'eau et de butanol (18/88) ; on ajoute 0,7 g. d'aniline. Après pulvérisation, le papier est maintenu à 105°C pendant 5 minutes (11). Les sucres se détachent en marron sur fond jaune.
- 2) Révélateur au NO_3Ag (12) adapté par L. SZABADOS (13). Ce révélateur nécessite la préparation de deux solutions :
 - a/ 1 ml d'une solution saturée NO_3Ag + 200 ml acétone
 - b/ 2 g. de Na OH dans 500 ml éthanol 90°.

- 2) Révélateur au NO_2Ag (12) adapté par L. SZABADOS (13). Ce révélateur nécessite la préparation de deux solutions :
- a/ 1 ml d'une solution saturée NO_2Ag + 200 ml acétone
b/ 2 g. de Na OH dans 500 ml éthanol 90°.

- a/ 1 ml d'une solution saturée NO_3Ag + 200 ml acétone
b/ 2 g. de Na OH dans 500 ml éthanol 90°.

- b/ 2 g. de Na OH dans 500 ml éthanol 90°.

L'électrophorégramme préalablement séché est trempé dans la solution (a). Il est maintenu à l'obscurité et à la température ambiante une dizaine de minutes. On le trempe ensuite dans la solution (b). Après l'apparition des taches brunâtres des glucides, l'électrophorégramme est lavé dans une solution d'ammoniaque, puis fixé par une solution d'hyposulfite de sodium. Il est à remarquer que le papier S + S 2043 a résisté mieux au deuxième révélateur.

L'ordre de migration est le suivant :

cathode rhamnose \rightarrow galactose \rightarrow glucose \rightarrow acide galacturonique
 \rightarrow acide glucuronique Anode

Contrairement aux résultats expérimentaux de la C.C.M., les acides uroniques migrent les premiers et se différencient assez bien.

L'étude des glucides par électrophorèse n'en est qu'à son début. Nous espérons donner des résultats plus complets ultérieurement.

LES LIANTS PROTEINIQUES

Les liants protéiniques (colle de peau, caséine, blanc d'oeuf) ont été étudiés en vue de leur reconnaissance éventuelle dans les encres d'Extrême ou Moyen-Orient (il y a en effet fort peu de probabilité de les retrouver dans des encres ferro-tanniques occidentales). Les résultats de ces expériences pourront peut-être servir également à l'identification des liants protéiniques des enluminures ou peintures.

L'hydrolyse s'effectue dans les mêmes conditions que pour les liants glucidiques mais dure 24 heures (2).

Chromatographie sur couche mince : elle est réalisée selon la technique mise au point au C.R.C.D.G. lors de l'étude des liants protéiniques des enluminures. On a utilisé un film Kodak 511 V (14) dont l'adsorbant est une résine de la classe des polycarbonates. On tamponne par trempage la chromatoplaque dans un tampon phosphate à pH 6,8 (pour un litre de solution tampon : KH_2PO_4 13,6 g + Na_2HPO_4 142g). Après séchage, activation de la plaque quelques minutes à 105°C et dépôt de l'hydrolysât, l'élution a lieu avec le mélange suivant (5) : Ethanol / eau / ammoniacque ; 85 / 13 / 2

Electrophorèse : on a utilisé le papier Schleicher Schnell 2040 b et un tampon de pH 1,9 ayant la composition suivante (16) :

acide formique / acide acétique / eau ; 26/120/1000

Dans ces conditions, les acides aminés se comportent comme des cations ; on les dépose donc le plus près possible de l'anode.

L'identification de tous les acides aminés d'un liant protéinique est malaisée vu la disproportion entre le nombre de ces acides et les microquantités de substances dont nous disposons pour les retrouver tous. Bien que délicate, la différenciation entre les différents liants (colle de peau, caséine, blanc d'oeuf), peut s'effectuer de la manière suivante grâce à une révélation en deux étapes* : cette révélation est valable à la fois pour les chromatoplaques et les électrophorégrammes.

- Dans une première étape, nous trempons la chromatoplaque ou la feuille de papier dans une solution contenant :

4 g. d'isatine + 40 ml d'acide acétique + 1000 ml acétone anhydre

Après un passage de quelques minutes de la chromatoplaque ou du papier à l'étuve à 105°C, les acides aminés colorés se détachent sur fond jaune. A ce niveau, nous prenons soin de bien répertorier la glycine, en notant d'une manière la plus précise possible son intensité.

- Nous procédons ensuite à la deuxième étape de la révélation très caractéristique de l'hydroxyproline.

* L'information émane de Mme FLIEDER

- La chromatoplaque ou l'électrophorégramme est trempé dans le réactif de Erlich (17). Celui-ci se prépare au moment de l'emploi 0,2g paradiméthylaminobenzaldéhyde+18 ml acétone+2 ml liCl concentré. Dans ces conditions, le fond jaune se décolore, les taches d'acides aminés également, sauf la proline (qui reste bleue) et l'hydroxyproline (qui devient rouge). Cette dernière est spécifique des collagènes animales ; sa présence exclut la caséine et le blanc d'oeuf. En cas d'absence de l'hydroxyproline, on différencie le blanc d'oeuf de la caséine par le fait que la glycine se trouve contenue en plus grande quantité dans le blanc d'oeuf.

Remarque - La deuxième étape de la révélation est très efficace pour différencier la proline de l'hydroxyproline dont les Rf sont très voisins en C.C.M. En électrophorèse, la séparation est très nette même en microquantité mais le réactif d'Erlich est employé systématiquement comme moyen de contrôle.

LES SUBSTANCES TANNANTES

Il existe deux classes de tannins : les tannins hydrolysables et les tannins condensés. Les tannins hydrolysables se subdivisent à leur tour en gallotannins (car par hydrolyse ils libèrent surtout de l'acide gallique) et ellagitannins (libération d'acides gallique et ellagique, celui-ci en plus grosse quantité).

Les tannins condensés de nature différente n'ont pas été étudiés pour le moment car ce sont surtout des tannins hydrolysables qui ont été utilisés dans la fabrication des encres (du moins selon les recettes répertoriées).

Les expériences ont été faites sur des substances naturelles (noix de galle de Chine, noix de galle de Turquie, écorce de grenade, gousses d'algarobilles, valonées, dividivi, myrobolan) concassées finement.

L'hydrolyse s'effectue dans les mêmes conditions que pour les glucosides ; elle libère des acides (gallique ou ellagique ou les deux) du glucose ainsi que d'autres substances supposées être des produits phénoliques.

Chromatographie unidimensionnelle sur couche mince : il semble qu'il ne soit pas nécessaire de neutraliser l'hydrolysât. L'adsorbant utilisé est le gel de silice, soit sur support de verre, soit sur support d'aluminium* sans ou avec indicateur de fluorescence (Merck 60 F 254). Après activation de la chromatoplaque quelques minutes

* Dans ce cas, on peut tamponner les plaques par trempage dans un tampon phosphate pH 6,8. Le tampon phosphate pH 8 est déconseillé car alors l'étape suivante qui est l'élution se fait très lentement.

à 105°C et le dépôt de l'hydrolysate, l'élution a lieu avec le mélange suivant (18-19-20) :

chloroforme - acétate d'éthyle - acide formique 5/4/1

Chromatographie bidimensionnelle sur couche mince : quelques expériences ont été réalisées en C.C.M. bidimensionnelle pour un cas précis : celui de la noix de galle d'Europe. Ce choix est justifié par le fait que la noix de galle est une des substances tannantes la plus fréquemment citée dans les recettes d'encre médiévales.

La chromatographie a été effectuée sur gel de silice étalée sur support d'aluminium.

Sans tamponner la chromatoplaque, et après activation et dépôt de l'hydrolysate, l'élution a eu lieu en utilisant le couplage suivant :

Eluant (A) : chloroforme / acétate d'éthyle / acide formique 5/4/1

Eluant (B) : isobutanol / acide acétique / eau 5/4/1

Nous avons permuté ces éluants comme suit :

éluant A $\xrightarrow{\uparrow}$ éluant B puis éluant B $\xrightarrow{\uparrow}$ éluant A

Electrophorèse : on a utilisé le papier Schleicher & Schnell 2040 b. Deux tampons ont été essayés :

tampon a) : pyridine - acide acétique - eau (100-10-890)

voltage : 2750 V ; temps : 30 minutes ; intensité 160 MA

tampon b) : tampon phosphate pH 6,3

(KH_2PO_4 7,24 g, Na_2HPO_4 4,77 g pour 1 litre solution tampon)

voltage : 3200 V ; temps : 30 minutes ; intensité 175 MA

Le dépôt de l'hydrolysate a lieu au centre de la feuille, car les produits de nature différente migrent pour certains vers l'anode, d'autres vers la cathode.

Deux révélations donnent de bons résultats :

1 - La première est valable pour les chromatoplaques et les électrophorégrammes : on pulvérise la plaque (ou la feuille de papier) avec de l'acide phosphomolybdique à 3,5 %, vendu en bombe pressurisée* (Merck, réf. 531) ; après passage à l'étuve quelques minutes à 105°C des taches bleues apparaissent sur fond jaune. En exposant la plaque (ou le papier) aux vapeurs d'ammoniac, le fond se décolore et les taches deviennent d'un bleu plus intense.

* Ce renseignement m'a été donné par Melle ROELOFS, Central Research Laboratory for Objects of Art and Sciences, Amsterdam. L'utilisation de la bombe évite la préparation de la solution méthanolique d'acide phosphomolybdique à 5 % signalée dans Kurt Randerath (20).

Remarques : - la tache du glucose met un certain temps à ressortir ; il est préférable d'attendre quelques heures avant d'interpréter les chromatogrammes et les électrophorégrammes. Cette tache du glucose une fois révélée reste d'un bleu très stable alors que les autres produits virent au brun.

- Si l'adsorbant contient un indicateur de fluorescence, un simple passage de la plaque aux UV (254nm) suffit. Les taches apparaissent en noir sur fond vert fluorescent.

- Même si on n'effectue pas de révélation, certains produits se révèlent d'eux-mêmes (en particulier l'acide gallique) au bout d'un certain laps de temps, sous forme de spots bruns sur fond blanc.

2 - Révélation au NO_3Ag (décrite ci-avant) valable uniquement pour les électrophorégrammes sur papier.

Résultats

En utilisant la C.C.M. ou l'électrophorèse, nous arrivons à séparer et à mettre en évidence de nombreux constituants, aussi bien en "macro" qu'en "micro" quantité, mais seul un petit nombre d'entre eux sont bien identifiés : glucose, acide gallique. En ce qui concerne la chromatographie sur couche mince bidimensionnelle utilisée pour la noix de galle d'Europe, les renseignements sont plus nombreux qu'en C.C.M. unidimensionnelle : le nombre de spots apparus après révélation est bien supérieur. Là une remarque semble s'imposer : en effet, une révélation au naphtorésorcinol (spécifique des sucres et absolument inactif pour les substances tanantes) effectuée après une C.C.M. bidimensionnelle montre au moins deux taches. Y aurait-il plus d'un sucre ou s'agit-il d'un dédoublement ? Pour le moment nous n'avons pas été plus loin dans nos investigations.

EXPERIENCES REALISEES SUR LES ENCREs

Bien que les techniques d'analyse mises au point sur les substances naturelles méritent d'être améliorées sur de nombreux points, il fallait vérifier la validité de certaines de nos méthodes en les appliquant aux encres, c'est ce que nous avons tenté de réaliser.

- Dans les encres ferro-tanniques préparées selon les recettes médiévales les plus classiques (noix de galle, sulfate de fer, gomme arabique ou miel), tous les ingrédients introduits ont été retrouvés et identifiés.

- Dans ces mêmes encres étalées sur papier et vieillies doucement en atmosphère chaude (87°C) et humide (60 % H.R.) pendant 4 jours il n'y a aucune modification dans les résultats.

- Devant ces observations somme toute assez encourageantes, nous avons prélevé des encres sur quelques fragments de manuscrits occidentaux datés écrits sur parchemin et datant des XIe, XIIe et XIIIe siècles.

- 10/10/5-11
- La recherche du fer est positive : toutes les encres en contiennent. Il s'agirait en première hypothèse d'encre ferro-tannique.
 - Pour la plupart, ces encres ont été fabriquées avec de la gomme arabique ou en tout cas avec un liant glucidique en accord avec ce que laissait prévoir l'étude historique préalable.
 - L'identification des substances tannantes pose encore des problèmes ; celles-ci ou ce qu'il en reste sont difficiles à retrouver.

CONCLUSION

Ce rapport n'est qu'une mise au point sur l'état des travaux effectués à ce jour dans l'identification des constituants des encres, à laquelle nous espérons apporter de nombreuses améliorations.

Pour les liants glucidiques, il faudrait continuer les travaux amorcés en électrophorèse et en C.C.M. bidimensionnelle pour arriver à une résolution beaucoup plus fine des problèmes qui se posent au niveau des liants, en particulier en ce qui concerne les acides uroniques.

Quant aux liants protéiniques, nous voudrions préciser que, si les essais effectués sur ces liants frais sont positifs, nous avons à vérifier la méthode sur les prélèvements de manuscrits :

- en premier lieu nous appliquerons notre technique aux enluminures de manuscrits : la couche picturale de ces enluminures étant une suspension de pigments organiques ou minéraux dans un liant protéinique entre autres. Ces analyses ont déjà été effectuées dans notre laboratoire en C.C.M. par Mme FLIEDER avec d'autres éluants d'autres révélateurs. Ce serait un excellent moyen de vérifier nos techniques, en particulier celle de l'électrophorèse puisque les résultats que Madame FLIEDER avait obtenus sont répertoriés.
- Ensuite, nous passerons aux prélèvements d'encre de manuscrits d'Extrême-Orient, celle-ci étant constituée, comme nous l'avons vu, d'un mélange de noir de fumée et de colle de peau, en général.
- En ce qui concerne les manuscrits occidentaux, la recherche des liants protéiniques ne se fera que si le liant glucidique était absent. Jusque-là ce ne fut pas le cas, toutes les encres contenaient, en accord d'ailleurs avec les recettes répertoriées, un liant glucidique.

Pour les substances tannantes, il s'agira dans un premier temps de reconnaître le plus grand nombre possible de constituants libérés par hydrolyse de substances tannantes et dont un petit nombre seulement sont identifiés.

Dans un second temps, il nous semble nécessaire de suivre la transformation chimique de ces composés dans le temps par l'artificialité du vieillissement artificiel, celui-ci devant être réalisé aussi bien sur des solutions tannantes que sur des encres préparées par nos soins. Ceci permettrait peut-être de mieux comprendre l'évolution des encres des manuscrits dans le temps.

Comme cela a été signalé dans le précédent article (1), cette connaissance de l'évolution chimique des encres permettrait d'arriver à déterminer avec le maximum de précision les constituants résiduels de l'encre, tels qu'on les trouve sur les documents. Ceci est d'une importance capitale si on veut prévoir les réactions secondaires qui peuvent se produire à la suite d'un traitement de restauration.

Centre de Recherches sur la
Conservation des Documents Graphiques
Paris

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Quelques détails pratiques sur l'électrophorèse

Les expériences d'électrophorèse ont été pratiquées sur un appareil CAMAG pouvant atteindre une haute tension (jusqu'à 5000 volts). Les produits à séparer sont déposés sur une feuille de papier (20 cm x 40 cm). La nature du papier choisi varie en fonction des éléments qui sont à étudier. Les dépôts des substances en solution s'effectuent à l'aide d'une micropipette de préférence sous forme de traits de 1 cm de long. Comme en C.C.M., on sèche entre chaque dépôt à l'aide d'un sèche-cheveux, de manière à accélérer l'évaporation et réduire la surface des spots. La feuille de papier est ensuite imprégnée de tampon ; il faut manipuler avec beaucoup de soin afin d'imbiber la zone où sont déposées les substances sans pour cela provoquer un étalement des taches ; de ce fait, on mouille les deux parties qui encadrent la zone de dépôt et on laisse le tampon arriver jusqu'aux spots par capillarité.

Si la feuille de papier est trop imbibée de tampon, on ôte l'excès entre deux feuilles de papier filtre (sinon le courant électrique traversera trop vite le tampon qui imprègne le papier sans pour cela entraîner une bonne séparation des produits). Le papier d'électrophorèse ainsi préparé sera soumis à une différence de potentiel allant jusqu'à 5000 volts. Les substances déposées une fois la tension branchée migrent alors vers le pôle + ou - du montage.

Lorsque nous n'avons aucune idée du sens de migration des produits à séparer dans un tampon donné, ceux-ci sont déposés au milieu de la feuille de papier. Lorsque le sens de la migration est connu, nous déposons les produits vers l'extrémité opposée au pôle vers lequel ils vont migrer. Le poids moléculaire des produits à séparer, leur charge, la force ionique et le pH du tampon, la nature du support, jouent tous un rôle important pour la bonne réussite d'une électrophorèse.

ESSAIS PHYSIQUES, CHIMIQUES ET BIOLOGIQUES DE PAPIER
JOURNAL ET DE PAPIER COUCHE. MÉTHODOLOGIE

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La composition des documents graphiques est telle qu'elle pose de nombreux problèmes de conservation et de restauration tant pour le présent que pour l'avenir.

Afin d'avoir suffisamment de connaissances pour - pouvoir affronter ces problèmes, le Service Espagnol de Restauration des Livres et des Documents a commencé une catalogage - et une étude sur les caractères physico-chimiques et biologiques appliqués actuellement aux papiers et aux encres.

Dans ce travail on expose les résultats obtenus - des différents essais effectués avec plusieurs produits sur ~~deux~~ ux papiers - Papier journal et couché - qui sont d'un grand intérêt et les plus fréquemment utilisés pour la documentation - graphique.

75/15/10-2

Conscient de la dégradation d'une grande partie du matériel qui, aujourd'hui, donne sa forme physique au document graphique et vu les difficultés qui se présentent une fois venu le moment d'appliquer une méthode conséquente de conservation et de restauration, le Service espagnol de Restauration des Livres et des Documents a lancé un programme de recherche qui tente d'analyser le comportement physique, chimique et biologique de ce matériel et sa réaction particulière à l'application des traitements préventifs et curatifs les plus courants.

D'une façon systématique, il a été prévu une série d'épreuves portant sur les papiers, les encres, le matériel photographique, etc. dans le but, en premier lieu, d'identifier leurs caractéristiques particulières et ensuite, après les essais, de confirmer, d'écarter ou, s'il y a lieu, de modifier les systèmes actuels de conservation et de restauration qui, en définitive, essaient de sauvegarder pour l'avenir la documentation graphique de notre époque.

Bien que ce programme ait débuté il y a deux ans, - il ne nous est pas possible de présenter un travail complètement achevé. Néanmoins, même dans ces conditions, nous considérons qu'il est intéressant d'exposer les quelques résultats obtenus jusqu'à présent en ce qui concerne le papier journal - et le papier couché.

Il nous faut signaler que ces résultats sont provisoires vu que le facteur temps ne nous a pas permis, pour certains aspects déterminés, d'atteindre un nombre suffisant d'essais aboutissant à des résultats concluants.

METHODOLOGIE.

L'hétérogénéité des différentes épreuves qui doivent permettre d'atteindre ce but incitait à établir, dès le début, une nomenclature générale où trouveraient place tous les traitements, produits, combinaisons, concentrations, etc. et où — les essais physiques, chimiques et biologiques seraient mis en parallèle. Cette nomenclature englobe, en principe, un processus théorique de conservation et restauration dans lequel il a été attribué une lettre à chaque traitement; cette section — utilise, corrélativement, un classement numérique, chaque chiffre correspondant à un produit déterminé. Le tableau que nous avons mis au point pour le moment comprend en tout quatorze — traitements et quarante-deux produits différents.

L'avantage que ce système apporte est qu'il pourrait être un langage d'une valeur universelle.

Le tableau ci-après concernant les essais que nous sommes en train de réaliser avec le papier journal et le papier couché et que nous présenterons ensuite, donne un exemple de — cette nomenclature qui, répétons-le, est commune aux divers matériels analysés ou à analyser.

Echantillon	Traitement	Produit
A	Contrôle. Sans aucun traitement	
B	Désinfection-désinsectisation	
B 1a	" "	Oxyde d'éthylène
B 1b	" "	" (15%)+CO ₂
B 1c	" "	" +Fréon
B 2	" "	Formol
C	Nettoyage (à sec)	

75/15/10-4

Echantillon	Traitement	Produit
D	Fixation de substances solubles	
E	Lavage	
E 1a	"	Lissapol (8%)
E 1b	"	" (15%)
E 2	"	Teepol
F	Elimination de taches	
G	Blanchiment	
G 1	"	Chloramine T
G 2	"	Hypochlorite de sodium + hypo—sulfite.
G 3	"	Peroxyde de H ₂ + éther
G 4	"	Permanganate de potassium + métabisulfite de sodium
H	Neutralisation	
H 1	"	Tétraborate de sodium
H 2	"	Carbonate de — magnésium
H 3	"	Carbonate de — calcium
I	Lubrification	
J	Consolidation	
J 1	"	Méthylcellulose
J 2	"	Nylon soluble
K	Réintégration	
L	Lamination	

Echantillon	Traitement	Produit
L 1	Lamination	Acétate de cellulose
L 2	"	Polyéthylène
M	Encapsulage	
M 1	"	Acétate de cellulose
M 2	"	Polyéthylène

CONTROLE DU MILIEU

des
 Pour parvenir à résultats homogènes, la constance -
 des moyens est indispensable. Dans notre cas, nous avons dis-
 posé de trois laboratoires qui sont utilisés chacun à des fins
 exclusivement physiques, chimiques ou biologiques et où le mi
 lieu ambiant présente les caractéristiques constantes suivan-
 tes:

humidité relative: 45-55%

température: 18-21°C

éclairage: 250 lux, avec écrans filtrants et dif-
 fusants

filtres antipollution dans le système de climatisa-
 tion

meubles métalliques anticorrosifs avec revêtement -
 en matière céramique antiacide

sols et murs avec revêtement plastique non poreux

INSTRUMENTAIRE APPLIQUÉ

Biologie

-Microscope Zetopan avec système de contraste de phase

-Microscope inversé Nikon avec système de contraste de phase

75/15/10-6

- Loupe stéréoscopique Nikon
- Matériel de microphotographie Nikon
- Vitrine de stérilisation
- Autoclave
- Compte-colonies
- Serre de culture Mermer

Chimie.

- Microscope Diapan Reichert, Zeiss
- Loupe stéréoscopique American Optical et Zeiss
- Matériel de microphotographie Reichert
- pH-mètres à contact et à solution: Corning de Bekman et Seybold
- Agitateur magnétique Selecta
- Balance de précision
- Chambre de vieillissement humidité-température Sapastin
- Centrifugeur Janetzki
- Vitrine pour déterminer la dégradation produite par la lumière UV et INF

Physique.

- Dynamomètre Creusot-Loire
- Appareil d'étude de pliure Creusot-Loire
- Appareil d'étude de rigidité Creusot-Loire
- Micromètre Creusot-Loire
- Appareil d'étude de déchirement Creusot-Loire
- Collagimètre Creusot-Loire
- Eclatomètre Creusot-Loire
- Incinérateur Creusot-Loire
- Balance pour cendres Creusot-Loire

ANALYSES BIOLOGIQUES-CHIMIQUES-PHYSIQUES.

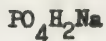
Les échantillons choisis, d'un format de 10 x - 150 mm, sont maintenus dans des conditions identiques pour les différentes épreuves et analyses.

Analyses biologiques.

Jusqu'à présent, elles ont consisté à faire les - essais suivants:

- I. Influence de l'humidité sur la contamination par les champignons et les bactéries
- II. Croissance spontanée des champignons et des bactéries
- III. Croissance contrôlée du champignon *Aspergillus tamarii*
- IV. Contamination fongico-bactérienne avec des matériaux - traités selon les produits de restauration.

Dans le premier cas, il a été utilisé des tubes à - essai contenant des solutions saturées de:



qui, avec une température constante de 20°C, ont fourni une - échelle de valeurs d'humidité relative de 63%, 76%, 84%, 92% et 100%.

Dans le second essai, après élimination de la conta- mination superficielle des échantillons avec de l'eau distillée stérile, les éprouvettes ont été placées sur un milieu de cul-

75/15/10-8

ture "agar-ozapek", contenu dans des plaques Petri. Pendant l'incubation à 30°C, il a été procédé à des contrôles de la croissance microbienne sur les échantillons de papier, les lectures étant effectuées les 1er, 3ème, 5ème, 7ème et 15ème jours.

Le troisième essai a consisté à observer la contamination provoquée par un mycète cellulolytique inoculé aux échantillons des différents papiers. Le champignon choisi était l'*Aspergillus tamaris*, inoculé au moyen d'une suspension de spores.

Voir les graphiques n° 1, 2, 3 et lames n° 1, 2, 3.

Analyses chimiques.

Ces analyses ont été axées sur les aspects qualitatif et quantitatif des échantillons à l'étude.

Le microscope a permis d'observer les différentes fibres en utilisant le réactif de Herzberg. Les types suivants ont été trouvés:

papier journal: mélange de pâtes blanchies et non de bois, de pailles, de sparte et d'autres fibres en moindre quantité;

papier couché: fibres blanchies de conifères et couche de cristaux de sépiolithe et de kaolin.

Par ailleurs, il a été procédé à un contrôle des variations de pH avant et après les traitements réalisés.

Voir le graphique n° 4 et lame 4.

Analyses physiques.

Après avoir fait subir aux différents échantillons - les divers milieux et procédés chimiques et biologiques, on - est passé aux essais physico-mécaniques dans le but de détermi-
ner le coefficient d'augmentation ou de diminution de leurs ca-
ractéristiques d'origine.

Les coefficients de résistance à la traction, à la -
pliure et à l'éclatement, la variation de poids et de volume,
etc. reflètent, en fin de compte, les pertes ou les améliora-
tions enregistrées par les matières en question à la suite de
l'application des différents traitements préventifs au cura-
tifs.

Voir le graphique 5.

CONCLUSIONS

Lors des essais biologiques, nous avons pu observer que si le papier journal est plus vulnérable à l'invasion microbienne, le papier couché manque davantage de défenses après avoir été traité avec les différents produits utilisés pour sa restauration.

Il faut remarquer l'effet inhibiteur des détergents et la contamination supérieure des échantillons traités avec des neutralisants à pourcentage alcalin élevé.

Quant à l'influence de l'humidité dans le développement des micro-organismes soit par effet spontané soit par - inoculation, on constate une similitude des résultats, le papier couché ayant tendance à être légèrement plus vulnérable.

Il faut mettre l'accent sur l'effet protecteur de - l'encapsulage. Par contre, dans la lamination, on constate - une contamination microbienne dans les coupes latérales de - l'échantillon. Ces essais relatifs au binôme humidité-contami- nation ont de nouveau confirmé l'effet positif des détergents et l'effet négatif des traitements avec des neutralisants - très alcalins.

Du point de vue chimique, les variations de pH su- bies par les différents échantillons sont acceptables sauf - lors du traitement de blanchiment à base de permanganate de potassium et de métabisulfite de sodium, par la dégradation - que subit le papier en raison de l'indice élevé d'acidité. — Dans le papier couché, la tendance à l'augmentation de l'alca

linité de départ peut faciliter les altérations microbiologiques ultérieures. Cela dit, il nous faut remarquer que cette alcalinité est fonction du revêtement minéral d'un papier à - prédisposition acide.

Les essais physico-mécaniques expriment l'augmentation des variantes subies par le papier, soumis aux différents traitements de restauration; donnant dans l'ensemble une idée du positif ou du négatif des produits employés.

Toutes les conclusions auxquelles nous sommes — actuellement arrivés, correspondent à des étapes déterminées du processus de restauration, dans l'attente de pouvoir obtenir des résultats définitifs concernant le traitement total — le plus adéquat de restauration depuis le triple aspect physico-chimico-biologique.

A cet effet, nous sommes en train de faire actuellement une série d'analyses unitaires et multifactorielles de — tous les produits employés dans notre Centre.

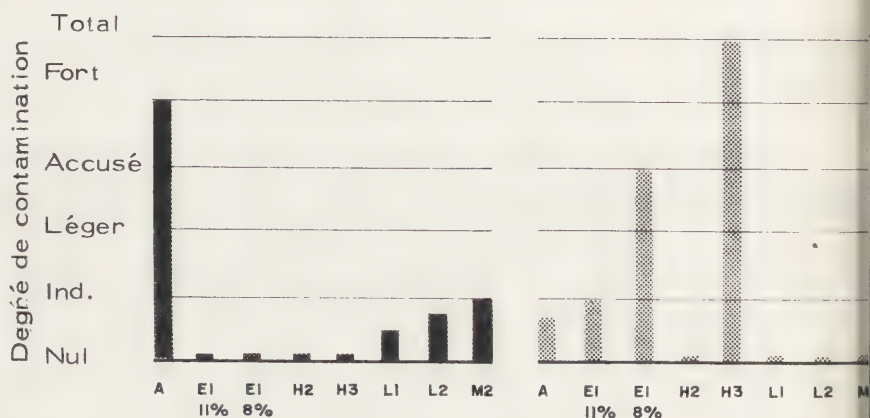
75/15/10-12

GRAPHIQUE n° 1

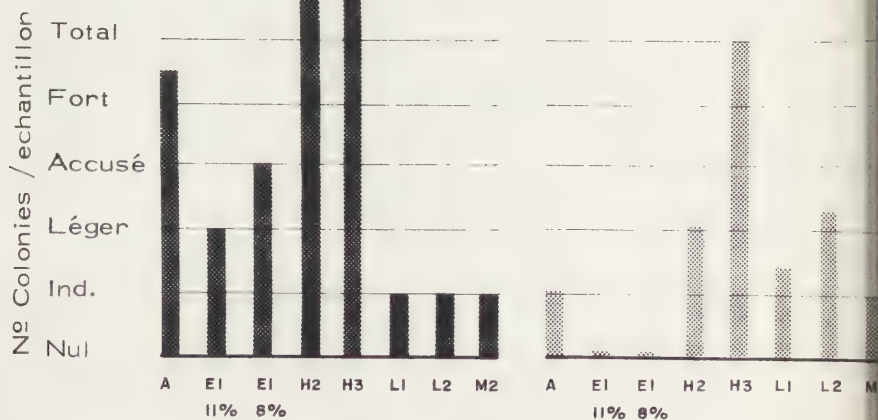
PAPIER JOURNAL

PAPIER COUCHÉ

Contamination bactérienne



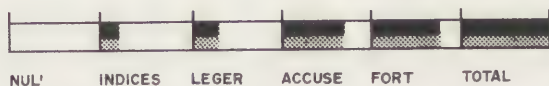
Contamination de champignon



GRAPHIQUE n° 2

INFLUENCE DE L' HUMIDITE DANS LE GRANDISSEMENT DE
MICRO-ORGANISMES SUR PAPIER JOURNAL ET PAPIER COUCHE

		TEMPS D' INCUBATION		HR. a T. de 20° C.				
			63 %	76 %	84 %	92 %	100 %	
A	3 SEMAINES							
	7							
	12							
Contrôle inoculé	3							
	7							
	12							
E1 Lissapol	3							
	7							
	12							
H2 Carbonate calcique	3							
	7							
	12							
H3 Carbonate magnésique	3							
	7							
	12							
L1 Laminé avec Acétate de cellulose	3							
	7							
	12							
L2 Laminé avec Polyéthylène	3							
	7							
	12							
M1 Capsulé avec Acétate de cellulose	3							
	7							
	12							
M2 Capsulé avec Polyéthylène	3							
	7							
	12							



PAPIER JOURNAL

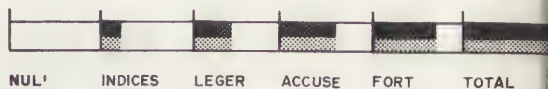
PAPIER COUCHE

75/15/10-14

GRAPHIQUE n° 3

INFLUENCE DE L'HUMIDITE DANS LE GRANDISSEMENT D'UN
CHAMPIGNON ASPERGILLUS TAMARI, INOCULE SUR DES E-
CHANTILLONS DE PAPIER JOURNAL ET PAPIER COUCHE.

		TEMPS D'INCUBATION		HR. a T. de 20°C.				
				63 %	76 %	84 %	92 %	100 %
A Contrôle inoculé	3 SEMAINES							
	7							
	12							
E1 Lissapol	3							
	7							
	12							
H2 Carbonate calcique	3							
	7							
	12							
H3 Carbonate magnésique	3							
	7							
	12							
L1 Laminé avec Acetate de cellulose	3							
	7							
	12							
L2 Laminé avec Polyéthylène	3							
	7							
	12							
M1 Capsulé avec Acetate de cellulose	3							
	7							
	12							
M2 Capsulé avec Polyéthylène	3							
	7							
	12							

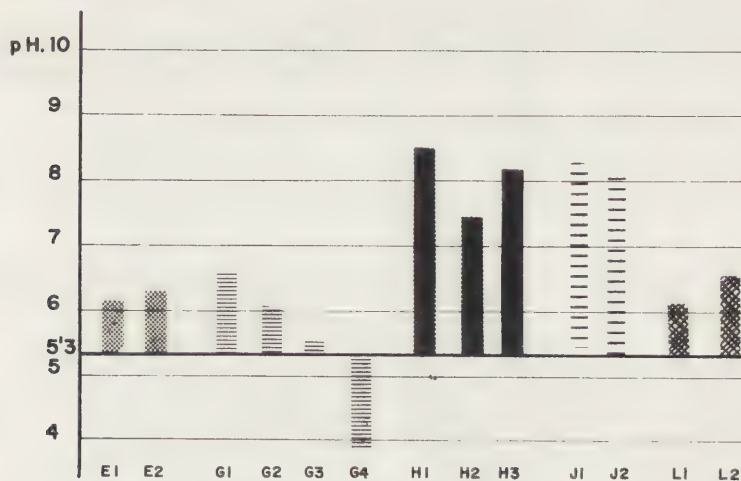


PAPIER JOURNAL

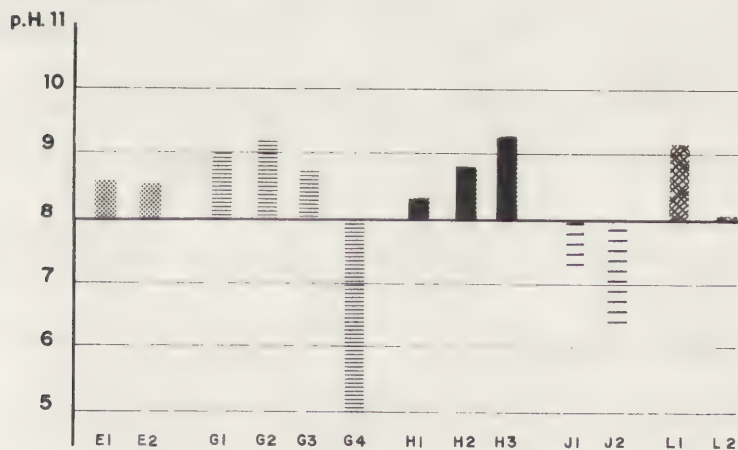
PAPIER COUCHE

GRAPHIQUE n° 4

VARIATION DU pH, SELON LES DIFFERENTS TRAITEMENTS.

PAPIER JOURNAL

5.3 pH ECHANTILLON CONTROLE

PAPIER COUCHE

8 pH. ECHANTILLON CONTROLE

GRAPHIQUE n° 5

VARIATION DU % DANS LE GRANDISSEMENT (+) O REDUCTION (-) DES
VALEURS PHYSIQUES DU PAPIER JOURNAL ET DU PAPIER COUCHE, -
APRES CHAQUE TRAITEMENT.

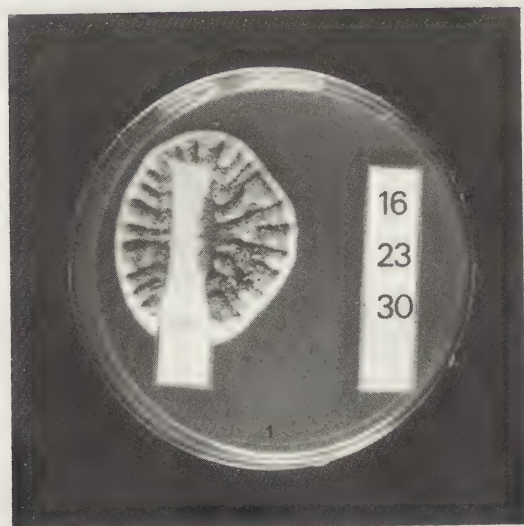
	E1	E2	G1	G2	G3	H1	H2	H3	J1	J2
Epaisseur	+ 62.79 18.6	62.79 18.6	62.79 18.6	60.79 18.8	50.2 8.4	55.3 8.4	62.79 16.9	62.79 16.4	48.9 8	50.82 8
Grammage	- 3.11 37.4	1.18 38	0.406 38	3.02 37.6	2.8 50	3 51.4	3.59 36.8	6.36 44.8	2.8 50.01	2.9 44.8
Poids spécifique	+ 3750 45.5	39.07 45.9	35.94 35.9	38.01 52.7	28.1 54.8	30.89 41.3	35.44 44.4	34.38 37.9	32 30.7	30.2 40.7
Indice volume	+ 60.25 88.4	64.10 89.9	55.11 89.4	53.2 115.6	43.9 78.2	50.60 78.2	55.76 83.6	51.28 127.8	52 84.6	49.8 78.2
m ³ /gr.										
Charge rupture	+ 35.72 9.4	22.17 2.3	19.20 8.7	16.2 22.8	10.59 22.8	10.59 22.8	13.40 0.00	11.17 37.9	19.9 25.7	20.8 16
* Longueurs rup-	+ 138.6 138.6	138.6 138.6	138.6 138.6	117.9 117.9	137.2 137.2	140.9 140.9	116.1 116.1	86.4 86.4	41 221.8	21.2
ture	- 3741 3741	21.99 21.99	22.26 22.26	22.01 22.01	14.9 14.9	19.8 19.8	16.55 16.55	16.25 16.25	35 35	35
Prolongements	+ 7.50 28.4	62.40 30.5	91.25 31.5	50.5 21	42.1 38.5	46.33 46.33	81.25 20.2	90 1.64	46.9 41.4	48.5 29.7
α	- 4.44 18.04	60 20.1	49.33 21.1	50.1 12.7	39.8 55.4	48.82 48.82	77.77 20.1	91.11 1.5	44.8 41.8	45.2 22.7
ε										
Travail choc	+ 20 5	20 5.1	28 31.8	27 8.3	19.2 85.8	232 32.3	20 8.1	20 30.58	25.1 44.1	24.1 32.3
Indice rigidité	+ 144.62 144.62	226.16 226.16	337.36 337.36	330.2 330.2	25.2 30.6	29.3 34.5	270.64 270.64	152.05 152.05	24.01 24.01	26.8 26.8
Module élasti-	- 41.78 94.3	22.63 94.8	3.73 33.1	3.50 88.7	3.1 85.2	3.2 91.6	11.50 9.46	40.50 86.4	2.9 92.8	2.89 96.3
cité	+ 799.2 799.2	398.5 398.5	1122 1122	799 799	123.8 123.8	573.84 573.84	12.43 12.43	640 640	1243.2 1243.2	467.1 467.1
Double plis	+ 76.96 76.96	49.31 49.31	45.17 45.17	48.6 48.6	39.6 39.6	43.59 43.59	44.71 44.71	46.56 46.56	10 10	40.8 40.8



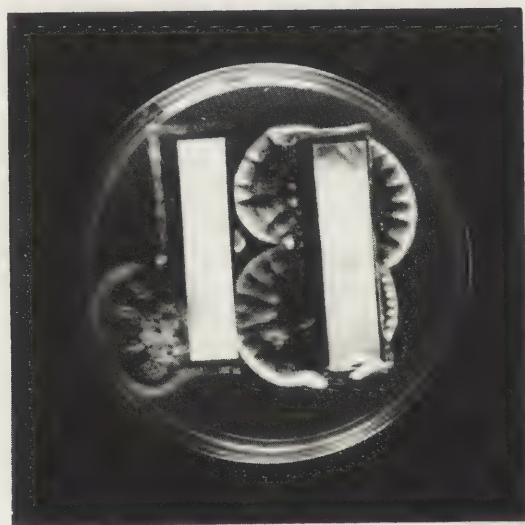
1.-) Papier journal sans traitement.-



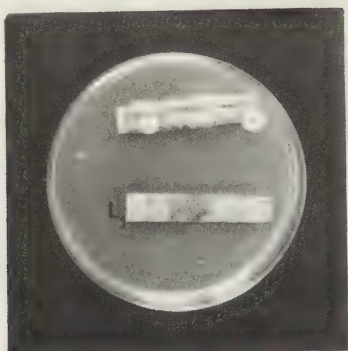
2.-) Papier journal traité avec Co_3Mg .-



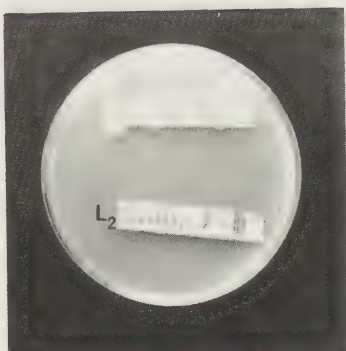
1.) Papier couché laminé avec polyéthylène.-



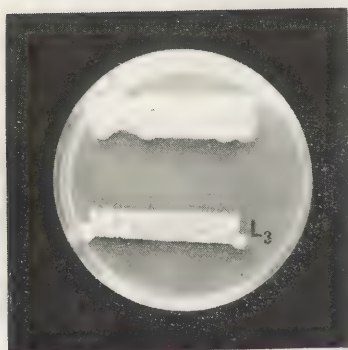
2.) Papier couché encapsulé avec polyéthylène.-



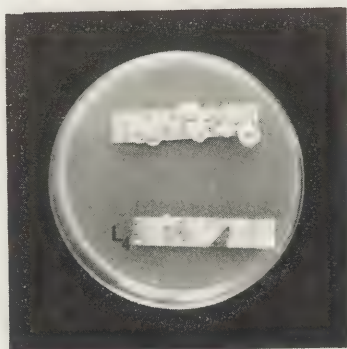
1.-) Echantillon traité
avec lissapol 100%



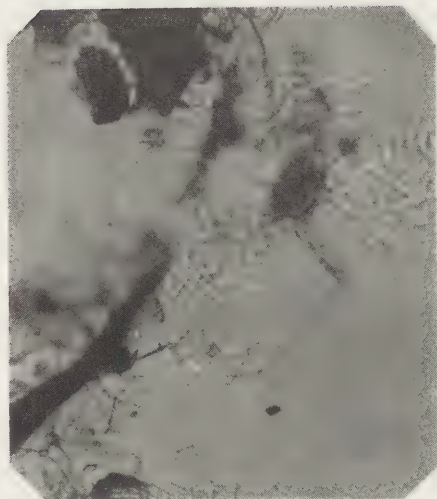
2.-) Echantillon traité
avec lissapol 25%



3.-) Echantillon traité
avec lissapol 15%



4.-) Echantillon traité
avec lissapol 11%



1.-) Cristaux de sepiolite, montmorillonite et Kaolin avec des fibres de résineux de papier couché. G = 100 X.



2.-) Cristaux de sepiolite, montmorillonite et Kaolin sur papier couché. G = 250 X.



3.-) Fibres de résineux de papier couché. G = 100 X.



4.-) Fibres de papier journal. G = 100 X.





PROBLEMS INVOLVED IN THE RESTORATION OF A MERCATOR ATLAS

Carlo Federici and Margaret Hey

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Abstract - the report, in two parts, describes the problems involved in the restoration of the 1623, 5th. edition, of a Mercator Atlas. The paper was extremely discoloured and acidic in nature. The coloured maps contained areas originally painted green which, now turning a deep chocolate brown in colour, have caused embrittlement of the paper, even its disintegration and loss. As the pigments of the maps are at least partially water-soluble, non-aqueous methods of restoration seem indicated. An investigation into the paper is described using, among other techniques, SEM combined with X-ray microanalysis. The presence of CaCO_3 , CaSO_4 , Fe_2O_3 , K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$ was determined and the crystals photographed. The implications of these findings in relation to the generally-accepted historical development of the use of alum in paper sizing is discussed together with the more serious implications of the presence of Fe_2O_3 . The advantages/disadvantages of attempting to remove iron compounds from old papers are summarised. The second part of the report discusses paper deacidification - what causes acidity, how it can be removed/neutralised and the latest research findings which underline the paramount importance of using calcium compounds for deacidification. A new non-aqueous method, involving the use of calcium acetate dissolved in ethanol is proposed and justified.

Résumé - le rapport, en deux parties, s'agit des problèmes qui se présentent dans la restauration de la 5^e édition (1623) de l'Atlas de Mercator. Le papier était extrêmement décoloré et de nature acide. Il y avait sur les cartes colorées des parties à l'origine verte mais qui deviennent brune foncée, ce qui rend le papier fragile et cause même la désagrégation et sa perte. Parce que les pigments des cartes sont, au moins en partie, solubles par l'eau, les méthodes non-aqueuses de la restauration doivent être employées. On décrit une investigation du papier, utilisant entre autres le SEM et la microsonde. La présence de CaCO_3 , CaSO_4 , Fe_2O_3 , K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$ fut déterminée et les cristaux furent photographiés. Les implications de ces découvertes à l'égard de l'histoire généralement entendue de la manufacture du papier sont discutées et aussi l'implication plus importante de la présence des sels du fer. Les avantages/désavantages d'essayer de retirer des composés de fer du papier sont résumés. La deuxième partie

du rapport s'agit de la déacidification du papier - qu'est-ce qui cause l'acidité, comment l'on peut la retirer/neutraliser et des découvertes les plus récentes de la recherche qui soulignent la nécessité suprême de l'utilisation des composés de chaux à ce but. Une nouvelle méthode non-aqueuse dans laquelle on utilise l'acétate de chaux dissolu dans l'éthanol est proposée et justifiée.

An investigation into the paper - Carlo Federici and Margaret May

Introduction - experience in Florence and elsewhere has shown that (fortunately) the paper in the majority of early printed books presents no technical problems in its restoration. However there is a large group of books which does present problems to which as yet we do not know the answers. These are loosely described as German-Swiss books of the 17th.-18th. centuries and are remarkable for the extensive discolouration of the paper which has occurred(1). Now it must be made clear that by this is not intended that discolouration found only on the printed area and variously attributed to oil from the printing block, iron or copper off-setting, again from the printing block, and so on. There are also problems to be clarified - but not at this moment. What is intended is that the discolouration has occurred all over the leaf or, if this stage has not yet been reached, that the discolouration is spreading, irregardless of the printed area and not always from the edges exposed to atmospheric pollution. Also it is not uncommon for only certain sections in a book to be affected, thus clearly linking the discolouration with the composition of the paper, rather than with any defects in printing or conservation. The discolouration is not always attended by enfeeblement of the paper, and closer study in Roman, Florentine and Dublin libraries has shown that by and large the problem shows itself in two distinct forms: a) the paper turns a yellow-orange brown in colour, it can be spongy in texture, but it is not very weak and will withstand washing; b) the paper turns a deep chocolate brown in colour, becomes excessively fragile, falling away, breaking up, even powdering in extreme cases and at this stage water cannot be used anywhere near the paper. This type of change is very reminiscent of that occurring when green copper pigments have been used on paper. The books studied from which these conclusions have been drawn represent only a small fraction of those possibly involved in these changes but so far the differences are very clear-cut. Many of the books were, in fact, printed in Germany but many also in Holland, which did not seem to fit the generally-accepted classification (a complete list may be obtained from one of us-M.H.). Only one analysis has, to our knowledge, ever been carried out on paper of this kind and copper was found(2).

The restoration of these books presents problems. If water treatment be possible bleaching is often carried out in an attempt to improve the colour. When water cannot be used the problem (together with the book!) is generally shelved. The idea of cellulose acetate lamination on these early books is not felt to be acceptable. We feel that the right choice of restoration treatment to be adopted when dealing with this, or any other type, of deterioration can only be made when the reason for the

discolouration and sometimes embrittlement be fully understood. The following is a description of some findings obtained from one of these books with this end in mind.

The book is the 5th., 1623, edition of the Mercator Atlas, printed in Amsterdam by Henrij Hondius (slide, title page). It is 46.5 cm. by 28.6 cm. in size, consists mainly of double-page coloured (in this edition) maps and, judging from the binding, has not been taken down in the past for restoration, although small local repairs to tears have obviously been carried out. The book was sent for restoration mainly because on the maps the areas originally painted green have discoloured, turning dark brown in colour and fragile in condition, even in places disintegrating and falling away as the leaves are turned (slide). Apart from this physical damage (green copper pigments) the paper of the book as a whole is incredibly discoloured being an orange-brown in hue. The paper is very thick, ranging from 0.53mm. to 0.29mm., curiously spongy in texture but not excessively weak in structure. Apart from the overall discolouration the paper presents a very mottled appearance, with sharply-defined spots, sometimes quite large, of a very dark brown-black colour. There are also very white, much more diffuse marks. Certain of the pages also show signs of having been brushed over, but very unevenly, with some liquid. In daylight these brush-marks show white in colour but under u.v. a strong purplish fluorescence (photograph 1, showing all these features; slide). The paper was suspected of being acidic.

The restoration problem consisted in need for consolidation of the green areas so that the paper could be handled without further loss. Since many of the pigments were water-vulnerable, neutralisation of any acidity and any general consolidation (or re-sizing) of the paper would have to be carried out in non-aqueous solutions unless all the pigments were to be fixed beforehand. Consolidation of the green-painted areas could be with heatset tissue (3), this being both water- and ethanol-resistant for short periods. Neutralisation of the acidity and protection against further acid development would be by using the calcium acetate method described later on, while sizing could be with an alcohol-soluble hydroxypropyl cellulose (3). It is hoped at the Conference to give further details of the restoration as actually carried out but before being able to begin this it was necessary to clarify certain puzzling features.

pH readings on the paper - extraction, 4.92 (water, double-distilled, 5.69)
contact, 3.65

after prolonged washing in hot distilled water the same piece of paper gave a contact value of 4.45

These values suggest considerable acidity linked to the cellulose structure and not removable with water.

Brightness values (TAPPI) ranged from 34.3 to 16.5. A paper sample (see above) after being well-washed in hot (40°C.) water showed no noticeable improvement in colour when compared with the page from which it had been taken, although a considerable amount of yellow material had been extracted.

Ash investigations - a small piece of weighed paper was ashed and the residue used for the determination of iron content. Effervescence on

addition of acid suggested the presence of carbonates. The iron content was determined spectrophotometrically and found to be 0.6%. Another very small piece of paper was ashed very carefully - just until the fibres had burnt away, the residue dispersed in distilled water and transferred to a piece of graphite foil for SEM investigations (see later).

Aqueous extracts - from the extraction pH measurements and washing experiments were concentrated. U.V. absorption curves of the concentrate showed the same pattern that had been obtained with artificially-aged samples(4).

Scanning electron microscopy

The samples were observed using a Cambridge Scientific Instruments Stereo-scan as in previous work(5), but this instrument, in the Dept. of Geology University of Rome (Professor R. Funicello) is fitted with an X-ray micro-analyser, enabling immediate analysis of any interesting features observed. Light elements (C, H, O, N, etc.) are not determined by this technique, nor very heavy ones, so that definitive analysis is not claimed. The paper samples were attached to the metal stubs using double-sided adhesive tape as before, but coating could not be with gold this time as it would have interfered too much with the analysis. Copper had to be excluded as being a possible component of the paper, so chromium was chosen.

Early results were exceptionally disappointing as it did not prove possible to identify any of the curious features remarked upon earlier. As brush-sizing of the paper was suspected, we wondered whether this was interfering too much by obscuring surface details so since the paper was so thick it was decided to split it, and try to see whether the inner surfaces thereby exposed would provide more information. All the comments/findings which follow relate to samples prepared from split paper, unless otherwise stated. In all the charts reproduced the chromium peaks are attributed to the metallisation and are therefore to be ignored. No attempt was made to determine, by using other metallic coatings, whether chromium was also present in the paper. On the photographs a black arrow indicates the point at which the analysis was carried out.

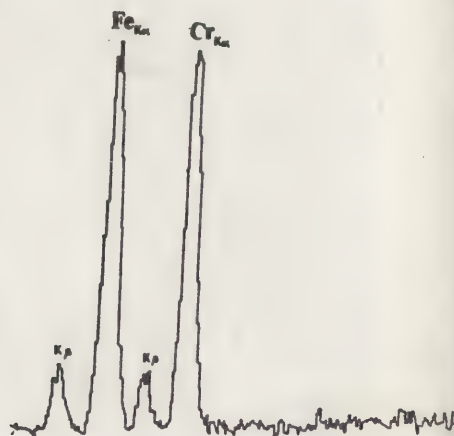
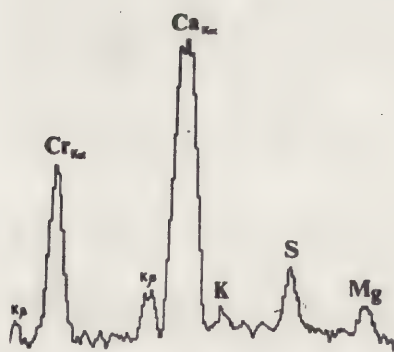
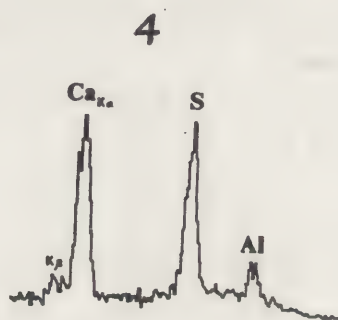
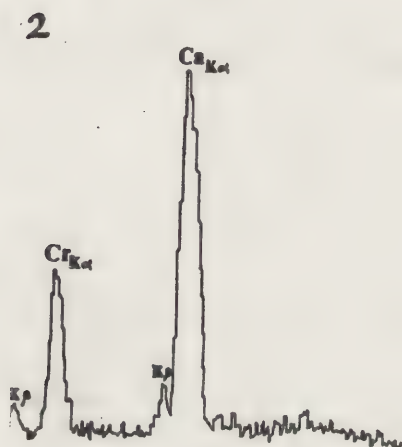
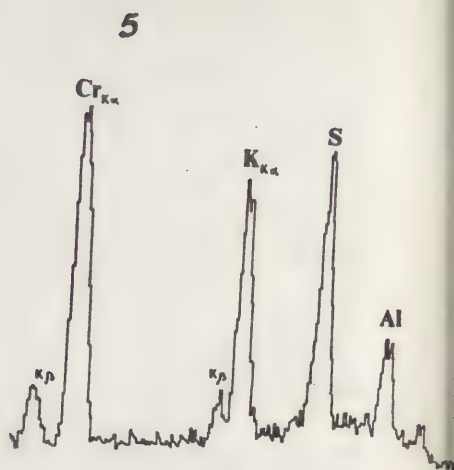
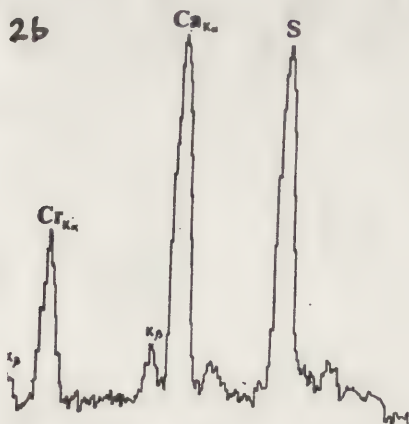
Photograph 2 shows a granule suspended between fibres. Analysis 1 indicates CaCO_3 , possibly also CaSO_4 with trace potassium and magnesium (as sulphates?) (slide).

Photograph 3 shows a cluster of oval granules encrusted on a fibre. Analysis 2a shows 80-90% calcium carbonate. The really exciting feature of this photograph is the occurrence of 'scales' to the right of the most compact granule. These, very well-known to restorers of outdoor marbles, statues, monuments, are calcium sulphate - analysis 2b (slides)

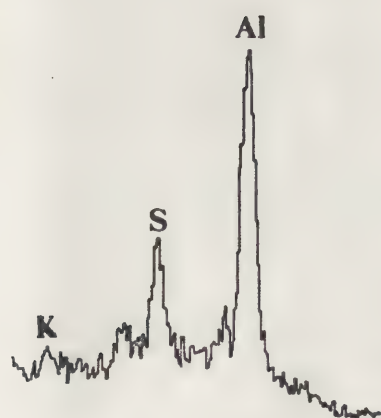
Analysis 3 - a small granule - ferric oxide

Analysis 4 - another granule, calcium sulphate with some aluminium impurity. Was this originally calcium carbonate, now sulphate through reaction with aluminium sulphate?

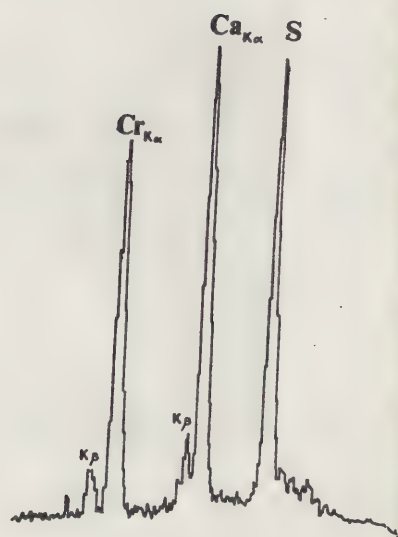
Analysis 5 - a small crystal containing K, Al - potassium aluminium sulphate?



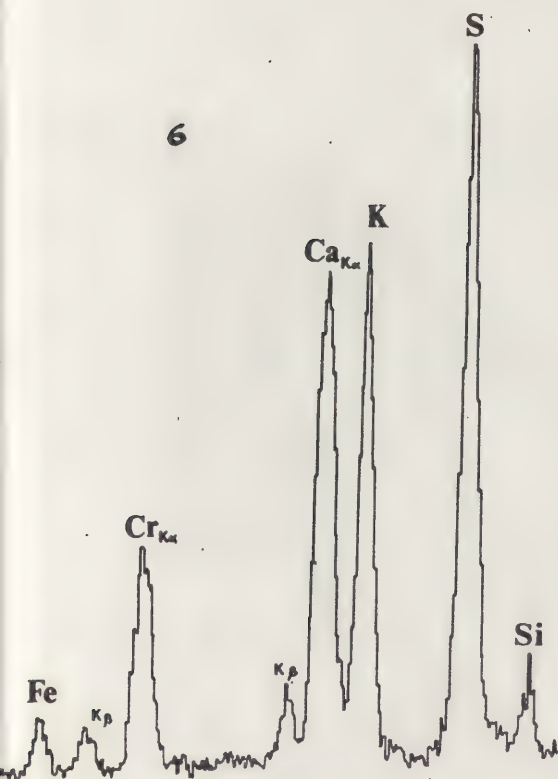
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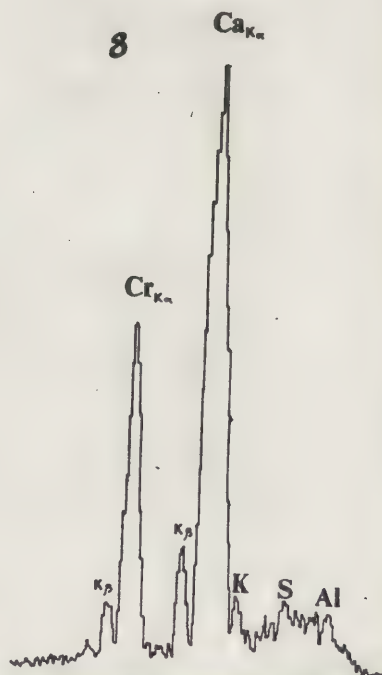
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6



8





Photograph 3, calcium carbonate - sulphate crystals, 5,000 times



Photograph 4 showing calcium carbonate (bottom lefthand corner)
and calcium sulphate crystals, 5,000 times

Analysis 6 - an inclusion of granular aspect, containing Ca, K, Li, S, Fe, which can be put together in various ways.

Analysis 7 - this was a very clear crystal, lying along a fibre. Unfortunately the photograph was lost through the camera being opened prematurely. The analysis indicates aluminium sulphate with some potassium also present.

Photograph 4 and the last two analyses were obtained in a completely different way. The dispersion in water of ashed paper (see earlier) dried on a piece of graphite foil was examined after metallisation. The very characteristic form of calcium carbonate (aragonite) observed in photograph 2 is again clearly seen in the bottom corner of the photograph. Obviously this form was not damaged by the ashing of the paper, nor dissolved in the water used to transfer the mixture to the graphite. The more soluble components of the paper are seen to have crystallised over and around these carbonate crystals from analysis 8. In the upper part of the photograph can be seen really beautiful crystals of calcium sulphate - analysis 9 (slides)

Conclusions - the preliminary investigations revealed the presence of some water-soluble acidity, but also considerable paper acidity as such, and a high iron content to the paper, obviously responsible for the discolouration not removable with water. The presence of some carbonates was also indicated. CEM/X-ray microanalysis confirmed the presence of precipitated iron, calcium carbonate, calcium sulphate and also showed clearly the presence either of aluminum sulphate as such or the more common potassium aluminum sulphate.

Calcium carbonate has been found in early papers by others (6;7) and is held responsible for the neutral-alkaline conditions in which so many of these papers exist even to-day (8). Despite its form water of manufacture is often held responsible for this alkalinity but as Williams (9) points out, if Hanson's findings of 2-3% are correct (7) of calcium carbonate, then some additional source, perhaps residual lime used to rot down the rags prior to paper manufacture, must be responsible.

The clear presence of alum in so early a paper (1623) is surprising. F.L. Hudson (10) refers us to the book 'L'Art de faire le papier', by de la Lande, 1761, where the use of alum in sizing was accepted as a practice of long-standing. D. Hunter (11) quoting the first European book to discuss the sizing of paper ('Papyrus sive ars Conficiendae Papyri', by J. Imbordiis Claramenti, 1693) does not mention the incorporation of alum into the size. Verner Clapp (12) quotes J. Evelyn's 1678 comments on its use in an English paper mill. Evelyn mentioned that 'gum' was added to the macerated pulp before sheet-forming and that the sheet before drying was dipped into an alum solution. Clapp felt that this was a mistake on Evelyn's part and that the alum was, in fact, added to the 'gum'/pulp mixture - but .. we wonder...

The date at which gelatine sizing as such was introduced into European paper making is now accepted as being around 1283 when, according to Gasparinetti (13) a paper containing gelatine had been used in Fabriano by Notaro Berretta. Gasparinetti quoted from a German translation by

Karabacek (Neue Quellen zur Papiergeschichte) of an Arabic book of the 1st. half of the 11th. century. Here is described how the Arabs used to size paper with rice starch or gum arabic, followed by surface treatment with an alum solution - see Evelyn's comments above.

Gasparinetti claimed that the Fabrianeze replaced these sizes with gelatine, readily prepared from parchment clippings and skin-off-cuts obtained from the tanneries which abounded in that area. He made no reference to the adoption also from the tanneries of the use of alum so it is not possible to say whether at that early date alum had already crept into paper-making. Barrow(14) in his survey of naturally-aged papers found that between the first and second halves of the 17th. century there was a drop in average pH values from 7.0 to 5.6 - which could indicate a change around that time in the materials being employed.

The presence of iron compounds in the paper is easier to account for - although the precise explanation will probably never be known. It could have been absorbed onto the cellulose from the water used at all stages of the paper's manufacture. Iron compounds are very common impurities in lime - perhaps this was the source, together with that for the calcium carbonate found? Then Hudson (op.cit.) draws our attention to iron impurities in alum - alum rouge - obtained from Smyrna, Turkey, since the 13th. century, while the monopoly in good quality alum - alum de Rome (Civitavecchia) - was held by the Vatican.

However perhaps rather more important is what is to be done about the iron in the paper. The most generally-accepted procedure is to attempt to remove it, using oxalic acid or a sequestering agent. One of us (N.B.) is not entirely in favour of this point of view. Much evidence exists(15) showing that iron compounds in large quantities do not damage cellulose especially when the concentration/form is such that the iron is precipitated as insoluble oxides, but that iron is extremely dangerous at very low concentrations or when in a soluble form. Oxalic acid and sequestering agents would both convert iron compounds into soluble forms and lower the concentration, probably into the danger level. Complete removal of the iron compounds would not be possible, since iron is very strongly attached to cellulose(16) and we think more careful work needs to be carried out on the problem and that for the time being, restorations procedures for the removal of iron compounds be discontinued, and certainly until indications we have(17) that the presence of calcium compounds nullifies the degradative effect of iron compounds be confirmed. If this be indeed so, then obligatory after-treatment with such compounds might permit the resumption of iron-removal treatments.

Apart from the chemical problems which a study of this book has brought to light, there are some fascinating technological ones related to sizing - we wonder, whether around the end of the 16th. century, knowledge of Arabic techniques became widespread, that originally brush-sizing with alum was employed, that being on the outer surfaces of the paper only some entered the inner paper structure. Perhaps later direct addition into the size itself was found less time-consuming - was it then that later damage to the paper was initiated? Or was it the gradually dying-out habit of rotting down with lime that was indirectly responsible? Was the alum, in earlier times, neutralised by the lime immediately?

Or is the real culprit the iron compound again linked with the presence of either calcium or aluminium compounds? Could it be that when calcium compounds are present the consequent alkalinity precipitates the iron as insoluble and therefore relatively harmless oxides? If on the other hand, there is no, or very little, calcium carbonate but acidic reacting alum, this could well retain the iron in a soluble very destructive form. Could this be the explanation for the severe degradation noted on some very dark papers? We do not know, but further analyses on other book papers are in progress. We should much appreciate some collaboration from scholars and archivists in tracking down, in the records of long-established paper mills, just when ~~mills~~ began to purchase alum in large quantities.

With regard to the possible source of the paper, especially in relation to the German-Swiss attribution of this problem of severely-discoloured papers - well, the guards, although of a type of paper very different from that used in the book, are also badly discoloured. The book paper has no water-marks that we can detect, but the guard papers carry water marks that were, according to Briquet, used by mills in Friburg and Sion. Also Voorn(18) describes how, around 1600, a Dutchman, Van Lockhorst, monopolised the trade with his dealings in Swiss and German papers, from the area around Basle. This trade ceased about 1635. It is interesting that the 10th. edition of this Mercator Atlas, also printed by Henrij Hondius, in 1630 and in Trinity College Library, shows certain differences. The paper is excellent, white, strong, in a superb condition, although some pages when held against the light show some yellow deposit within the paper structure. The maps are again coloured but the greens are a different pigment and no damage/discolouration is present. There is obviously much scope for investigations into different editions in connection with the contemporary paper trade. But meanwhile restoration must go on.

Non-aqueous deacidification - Margaret Hey

In order to be able to deal satisfactorily with restoration problems such as these, it is necessary to have available non-aqueous methods of treatment. For a short time it was thought that non-aqueous deacidification at least was a problem resolved with the publication of the Baynes-Cope barium hydroxide/methanol method(9). However, Williams' comments(9) on the toxicity of both working method and treated material have made us face up more clearly to what is involved when recommending for use in uncontrolled workshops any method/material which carries with it the slightest element of risk to personnel. Therefore the method must be discarded from restoration practice. It might seem that thereby a backward step is taken to pre-1969 conditions but in practice this is not so. During the intervening years independent work from two sources(20;4) and from two directions, has begun to clarify the fundamental problems involved in cellulose deacidification, so making the whole picture much clearer. But before being able to discuss this in detail it is necessary to be quite clear about what it is that the deacidification reaction is supposed to do.

Acidity in paper arises in 4 different ways:-

- a) from COOH groups produced either by the natural degradation of the cellulose or by its oxidation during bleaching procedures;
- b) from sulphuric acid produced from alum incorporated into the paper with gealtine(earlier) or rosin(later) sizing;
- c) from sulphuric acid produced by catalytic oxidation, by heavy metal(especially iron) impurities in the paper, of sulphur dioxide in polluted air;
- d) from sulphuric acid in iron gall inks. Although very serious when it occurs, since it leads to loss of written matter, the raison d'être of the manuscript/annotated book, it is nearly always local damage only.

Now acidity (b) will be removed by good water washing which hydrolyses the alum, and neutralisation with any alkaline solution. Therefore provided both these procedures be carried out conscientiously this source of acidity will be effectively removed during restoration and will not recur, provided alum not be added to the paper during its restoration.

Acidity (c) will also be removed during restoration. Its future re-occurrence will depend upon a) aerial pollution in the library concerned, and then b) the effectiveness with which the heavy metals in the paper can be prevented from exerting their catalytic action.

Acidity (d) is also a limited, non-recurring source of acidity which again should be totally neutralised by efficient restoration.

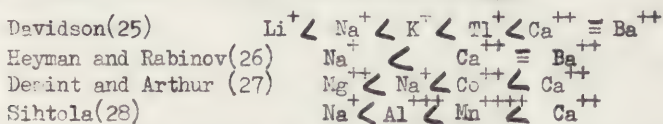
All these comments presuppose either prior washing of the paper concerned (always preferable) or the use of aqueous solutions when the soluble sulphates will be washed from the paper. Should the method actually adopted not involve water-washing then another factor comes into play and that is the stability of the sulphate produced. It is for this reason that the ammonia treatment is worthless- there is indeed an immediate increase in pH but the ammonium sulphate formed is unstable and with the passage of time the ammonia is released and free sulphuric acid is once again produced. The same reasoning of course applies to the use of any volatile alkaline compound, and again when using a non-aqueous method, since the sulphates produced will have only a limited solubility in the non-aqueous solvent employed.

But on the whole the problem of safely neutralising sulphuric acid in the paper is relatively simple and a variety of alkaline compounds will do this adequately and permanently. We are therefore left with acidity (a), that arising from the cellulose itself and this, in fact, is the fundamental factor involved. As removal of the sulphuric acid occurs immediately it is the effectiveness of the reaction with the carboxyl groups and the innocuity of the substance left behind in the paper after treatment which entirely govern the long-term consequences of any deacidification process. Unfortunately previous work on the subject has largely ignored this aspect of the problem. It is, of course, true that when dealing with modern rosin/alum sized papers, and especially when it is in books kept in heavily-polluted city libraries the damage caused by the sulphuric acid in untreated books far out-weighs any damage due

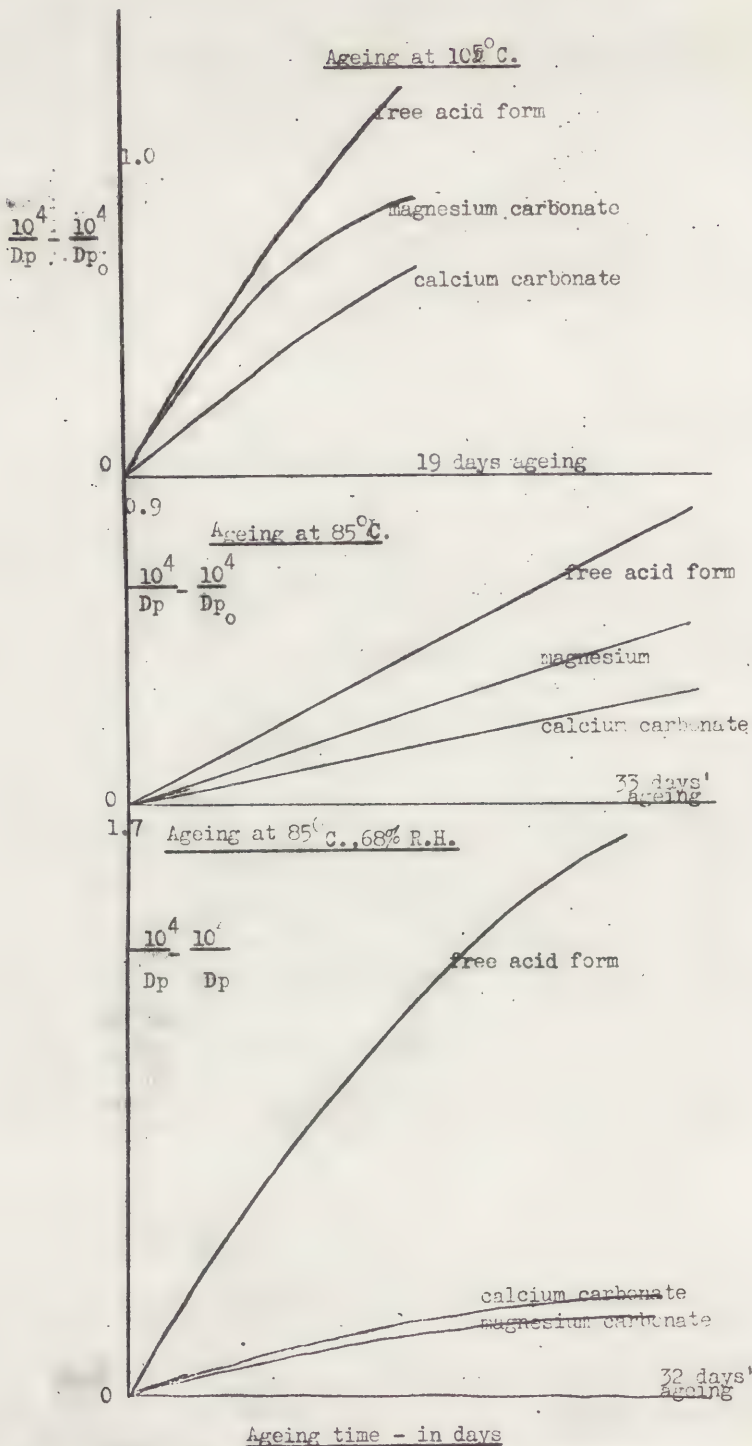
to the cellulose acidity alone. But, as I have tried to point out, this source of acidity will be removed during restoration. Then we must remember that the majority of paper treated in Europe is not rosin/alum paper - it is necessary only to think of Values 1,2 and 3 in Florence, and therefore the reactions between any alkaline solution proposed for use and cellulose itself must be given precedence.

The degradation brought about by the acidity arising only from free carboxyl groups in cellulose has been clearly demonstrated by Davidson (21) and Ant-Wuorinen (22) in work on cellulose as such; by Wilson et al (26) in connection with work on permanent-durable papers and by Hey (4) as the consequences of restoration procedures. Some of the results obtained in the latter work are shown graphically on the following page. The differences in behaviour, under three different sets of accelerated ageing conditions, between cellulose left in the free acid form, or previously neutralised either with pure calcium bicarbonate solution or pure magnesium bicarbonate solution, are clearly seen, and the degradation ~~caused~~ of the cellulose by the free carboxyl groups is evident. Philip and Baudisch found that cellulose degradation by free carboxyl groups increased with an increasing number of free carboxyl groups (23). Comparing the results obtained with calcium and magnesium treated samples, only calcium shows no differences in behaviour between dry and moist ageing at the same temperature. The notable degradation which occurs with magnesium-treated samples on dry ageing, together with the iron/magnesium interaction, which at certain concentrations can lead to even greater degradation (24) contribute to the decision that magnesium compounds must not be used as deacidificants. To this degradation must be added the fact that even on moist ageing when magnesium-treated samples behave very well, there is considerable yellowing of the cellulose (17) whereas with calcium-treated samples no discolouration occurs at all. The problem with the iron is so finely dependent upon the ratio Fe:Mg, and the actual concentration either of iron in paper under restoration or in quantity of magnesium deposited after restoration ~~that~~ would be impossible to determine, that on practical grounds nothing can be done. The apparent ability of calcium compounds to suppress the degradative effect of iron compounds at various concentrations (17) is an asset.

The paramount need is the ability to neutralise carboxyl groups and keep them neutralised - much work has been carried out on the relative ease with which metals ions are attracted to, and retained by, cellulose carboxyl groups. Some findings are the following:-



There is the common finding of the greater affinity of calcium for cellulose carboxyl groups over all the other common metals. Why this should be is uncertain - but could be linked with the complexing affinity of calcium ions with carbohydrate groupings - a reaction used in sugar purification and known since the 10th. century.



Thus treatment with calcium salt solutions is the most effective way in which cellulose carboxyl groups can be neutralised and kept neutral in the future. But now the question arises - is there any danger in the excess calcium carbonate which will be inevitably left on the paper - since it would be impossible for the restorer to treat a variety of papers with just sufficient calcium salt to neutralise the carboxyl groups and no more. The innocuity of any treatment depends upon the solubility of the material left behind in the natural water content of the cellulose, and then the reaction, if any, between the solution thereby produced and the cellulose. Taking the first part - the solubilities in water of the four carbonates proposed for use on paper are :-

in 100ml. H ₂ O - Na ₂ CO ₃	7.1 - 21.5 g.
BaCO ₃	0.0022 g.
MgCO ₃	0.0106 - 0.15 g.
CaCO ₃	0.0012 - 0.0014 g.

Of the four, only sodium carbonate would be likely to give a solution of appreciable concentration, and this would be a solution of sodium hydroxide. The degradative effect of sodium hydroxide solutions on cellulose is extremely well documented(29). The degradation occurring is directly proportional to the concentration of the carbonate present (17).

It could be said that low concentrations would not be harmful - this is questionable. Sodium salts, whatever their nature (sodium carboxymethyl cellulose; sodium salts of fungicides; sodium salts for deacidification) must never be employed on paper or other cellulose-based objects.

N.B. This is an embargo supported 100 % by W.K. Wilson !

Therefore we are left with the 'choice' of calcium compounds only to be employed for paper deacidification and protection. Aqueous solutions present no problems as either the hydroxide or calcium bicarbonate solution could be employed, ~~depending~~ depending upon the circumstances and nature of the material being treated(3). Non-aqueous possibilities seemed to present more difficulties.

Calcium acetate as a possible compound for use

I was continually coming across references in the literature to the use of calcium acetate in investigations into various facets of cellulose chemistry and degradation. These included the Sihtola work(28) work on cellulose yellowing (calcium-treated samples yellowed least of all); work on the base exchange properties of cellulose(27) and most appositely, all the work by Wilson et al from 1971 onwards was carried out using calcium acetate-treated cellulose in the confrontation with free acid form and the aluminium salt. The results obtained with the calcium-treated sample were eminently satisfactory. It therefore seemed to me that if I could use calcium acetate in a non-aqueous deacidification procedure, the published literature would be a justification for further investigations.

Unfortunately, calcium acetate is not soluble in ethanol as such, nor in 95% ethanol. But I found that by adding 2 ml water to the latter I could dissolve the acetate. In fact, the best way of working is to dissolve the acetate in the quantity of water to be added, then add the ethanol to

make up the required volume. The solution formed is absolutely clear and its stability would seem to be in the range of 2-3 days. As however, solubility in the water-ethanol is immediate, there is no need to store the solution. Having therefore obtained a solution I needed to know whether it would deacidify in practice. Some values for extraction pH after treatment are given in the Table. I found that when treating the very acid (with sulphuric acid) manuscript that the calcium sulphate formed during treatment turned the solution somewhat milky in aspect. No visible deposit of calcium sulphate could be seen on the paper after drying but should something similar be observed during restoration it would be advisable to prepare a fresh solution of calcium acetate and before drying them pass the sheets through this solution. This should be sufficient to remove all possibility of deposit formation on drying. It is absolutely useless to use ethanol alone for this purpose - it would remove the calcium acetate and so nullify the whole deacidification procedure - further explanations on this point are given elsewhere(3).

Some miscellaneous extraction pH values for papers treated with calcium acetate solutions

Whatman, untreated pH 6.70

treated, 0.02N CaAc

- pH (on drying) 6.86; after 36 hrs. 8.62

Whatman, as above

pH (after 24 hrs) 7.35; after 6 days 9.56

Calcium acetate 0.02N

<u>10 mins. immersion</u>	<u>initial pH</u>	<u>24 hrs.</u>	<u>96 hrs.</u>
4.78	4.78	6.87	7.13
	5.54	7.11	7.48
	6.30	7.28	9.10
<u>two treatments, 10 mins.</u>	4.78	7.70	9.01
	4.54	7.73	8.71
	6.30	7.43	8.96

Should there be any concern over the allegedly too high final pH values I would refer readers to what is said earlier - that the innocuity or otherwise of any treatment depends entirely on the solubility of the material left behind (in this case, calcium carbonate) and the reaction of any solution which could be produced on the paper by that material. I would also draw attention to the superb condition of the early papers said to contain 2-3% calcium carbonate - which would give extraction pH values at least as high, if not higher, than these.

Being rather satisfied with these results which showed that the solution did deacidify, it was necessary to carry out testing to demonstrate that in the restoration context as well as in the literature findings cited above, calcium acetate-treated papers were not degraded with respect to non-treated papers.

Four different test series were carried out, using the same test conditions as those employed for the work graphically reproduced, that is,

105°C., 85°C., and 85°C. and 69% relative humidity. For the first three of these test series all samples were aged only after having been left exposed to the air for at least three days, in order that the calcium acetate be fully converted to calcium carbonate. With ageing periods even as long as 39 days it was not possible to demonstrate any greater degradation in treated samples - see Table for some of the values. It seemed evident that degradation might only occur where the treated papers not to be exposed to the atmosphere, and therefore partly left with calcium acetate present. Therefore the final test series confronted samples which were left exposed to the atmosphere for 1 week with freshly prepared samples, put to age immediately and in sealed glass tubes, which would accentuate any degradative effect of acetic acid still on the paper. The results were as expected (see Table)

Table of some values obtained in the ageing series carried out

		<u>average degree of polymerisation</u>	
<u>ageing at 105°C.</u>		<u>initial</u>	<u>38 days ageing</u>
treated		1252	576
non-treated		1252	575
<u>ageing at 85°C.</u>			<u>39 days ageing</u>
treated		1252	1004
non-treated		1252	980

	<u>extraction</u>		<u>average degree of polymerisation</u>	
	<u>pH values</u>		<u>initial</u>	<u>17 days ageing</u>
	<u>initial</u>	<u>3 days ageing</u>		
a) untreated	6.43	5.68	1337	1025
treated, 6 days old	8.94	8.42	1337	1114
b) untreated	6.50	5.80	1337	1163
treated, fresh	7.08	5.27	1337	572

From these values it is clearly absolutely essential that any treated paper be left fully exposed to the atmosphere until the smell of acetic acid be fully dispersed. This takes place within 2 days and is very easily detected by the restorer - by just smelling the paper!

There is still a good deal of practical restoration work to be done on this method - especially with regard to its use on coloured material where perhaps the acetic acid released could affect some pigments. At the Conference it is hoped to give details of results obtained.

The method is not a cheap one to employ since it requires the use of ethyl alcohol, which in most countries is exceedingly expensive to purchase. However, it has the advantage over the barium hydroxide/methanol one (which is equally expensive to use) of being non-toxic.

75/15/11-18

The concentration suggested for use is 2 gm. per litre - this gives a solution about 0.025N - that is, half way between the two solution strengths employed in the above work. It is suggested that the solid be dissolved in 20 ml. water, and then brought up to volume with 95% ethanol.

M.B. - this was the solution employed in Italy - I need to carry out investigations into the mixtures to be employed when using the industrial spirits available in other countries. More details will be provided at the meeting.

We should both like to express our deep thanks to Signora Franca Manganelli, Head of the Restoration Department, Istituto di Patologia del Libro, Rome, for her interest in, and encouragement of, this work. One of us (M.H.) would also like to thank most sincerely the Director, Professoressa Bianca Galante, for the hospitality of her Institute where the chemical work described above was carried out.

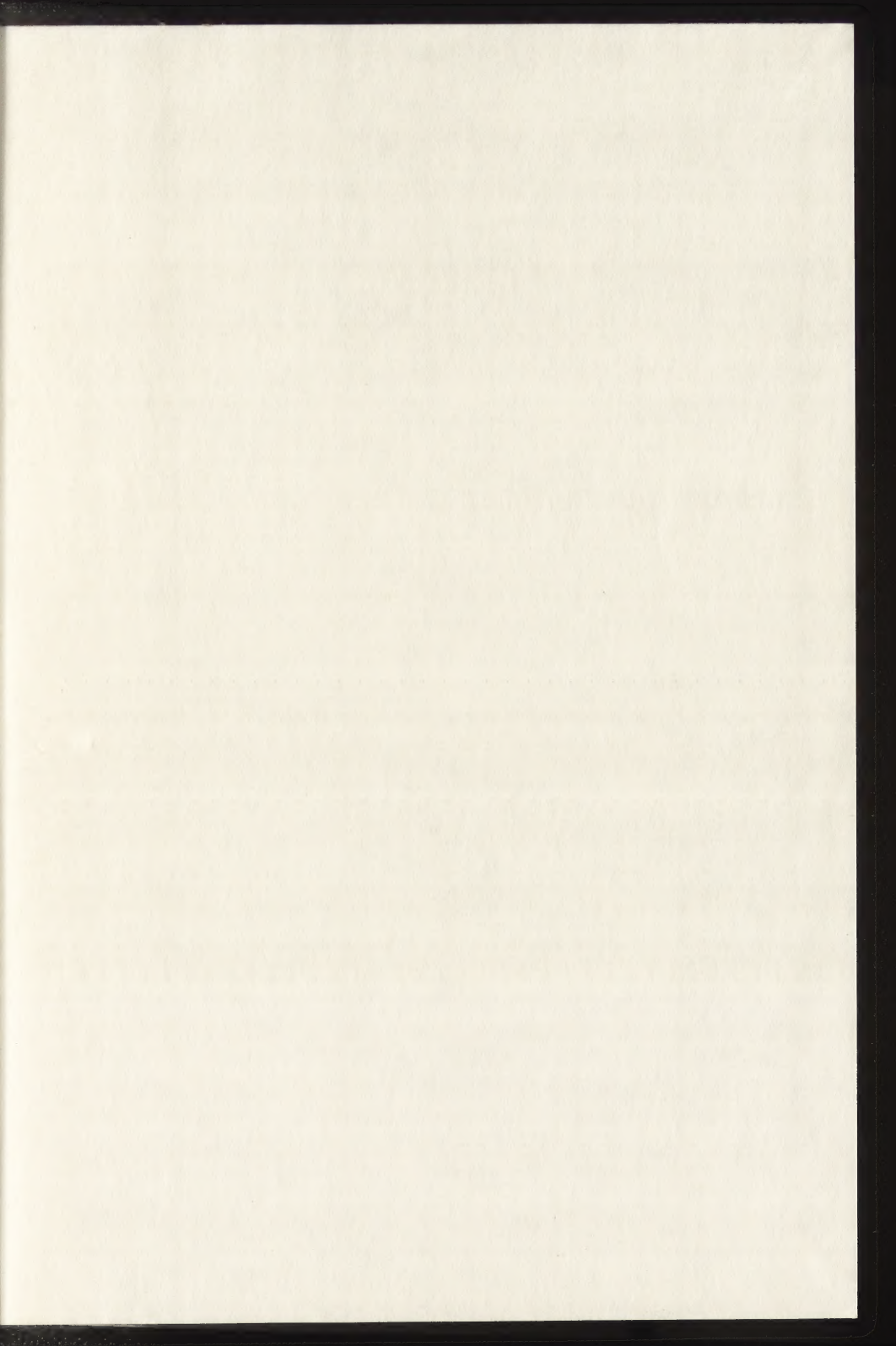
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